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Drying and re-wetting of organic wetland sediments: Biogeochemistry and implications for wetland management

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DRYING AND RE-WETTING OF ORGANIC WETLAND SEDIMENTS: BIOGEOCHEMISTRY AND IMPLICATIONS FOR WETLAND MANAGEMENT

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USE OF THESIS

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ABSTRACT

In the past decade, increasing instances of eutrophication and acidification of wetlands on the Swan Coastal Plain (SCP), Western Australia, and particularly on the Gnangara groundwater mound, have coincided with gradually decreasing ground- and surface water levels. The processes involved in determining whether a wetland will acidify or become eutrophic (or both) as a result of drawdown are still poorly understood, especially on the SCP where there are strong links between wetland water quality and underlying geomorphology. For instance, many of the wetlands located on the well-buffered geomorphic unit called the Spearwood dunes are eutrophic due to high nutrient loads, and drying appears to exacerbate this. On the other hand, many of the wetlands on the leached and poorly buffered geomorphic unit called the Bassendean dunes also have relatively high nutrient inputs but are not eutrophic, and drying appears to cause acidification. However, an increasing number of wetlands on the Spearwood dunes are now also becoming acidified due to lowered groundwater tables. All of these have organic-rich sediments, none of which have to-date been characterised for management purposes. Yet it is in these organic systems where observed responses to hydrological change, particularly to drawdown and drought, tend to be the most severe. The broad aim of this research was thus to identify and describe the overall effects of drying and rewetting on the biogeochemistry of organic-rich wetland sediments. The methodological approach was based on inferring biogeochemical processes from known relationships between measured variables as a means of improving our understanding of wetland function. The study site, Lake Goollelal, supports two distinct types of organic sediments: suspended detrital floc and peat. Both were found to be sulfidic and iron-rich. The floc was also very nutrient-rich. Analyses of elemental concentrations suggest that the peat organic matter is primarily of vascular plant origin, while the floc is of aquatic (algal) origin. Both sediments became severely water repellent when dried.

Slurries of dried/rewet and continuously wet sediments of both types were incubated under anaerobic and aerated conditions for 49 days. The main outcomes of these experiments were that aeration played a more important role than drying in the peat, while in the floc the opposite was the case. In the peat drying/rewetting had little effect on pH, phosphorus, sulfur, iron and calcium transformations under anaerobic conditions. Aeration however, resulted in the acidification of the continuously wet peat, and to a lesser degree of the dried peat. In the floc, drying significantly increased

phosphorus release under both anaerobic and aerated conditions. In short, in the floc drying caused eutrophication with recovery over time (however still significantly over pre-drying levels), while in the peat it caused perpetual acidification. Drying-induced water repellence had the significant consequences of retarding acidification and exacerbating eutrophication.

In order to help explain observed responses in the incubations of the sediments, two elemental fractionation schemes were carried out. In the peat, drying decreased the potentially mobilisable phosphorus fractions, probably due to increased phosphorus sorption capacity of the sediments. In contrast, drying substantially increased easily mobilisable phosphorus in the floc, the most likely reason for this being the very high amount of drying-induced mineralised phosphorus compared to iron (and aluminium) content of the floc. This was also interpreted as being the reason for the observed aerobic phosphorus release in the incubation study. The dominant iron and sulfur phases (representing between 70% to 90% of both total sediment Fe and S) were $KClO_3$-extractable (i.e. bound to organics and sulfides), and approximately half of this was chromium-reducible. The iron oxide pools, both 'free' amorphous and crystalline, were very small in both sediment types, with no observed drying-induced increase in crystallinity. The dominant calcium pool was sodium acetate-extractable (most likely $CaCO_3$). This pool represented only a fraction of that required to neutralise the acidity which could potentially be produced by the S_{KClO_3} pool. Yet in the aerated incubations of the dried floc, no acidification response was observed; indeed pH rose to >8. This demonstrated that chemical buffering capacity and biogeochemical buffering capacity are not the same thing. It is argued that which ever can override the other in response to disturbances will determine the resilience of the system. This has important implications for adaptive management of groundwater-dependent wetlands in drying environments. For adaptive management based on resilience to be effective the variables that determine or control the resilience of natural systems must be identified and understood. That detrital floc, and to a lesser extent peat, has escaped such characterisation on the Swan Coastal Plain highlights a lack of understanding of key wetland processes critical to wetland management.

DECLARATION

I certify that this thesis does not, to the best of my knowledge and belief:

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We forget that the water cycle and the life cycle are one.

- Jacques Cousteau

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CHAPTER 1
GENERAL INTRODUCTION: GROUNDWATER DRAWDOWN AND BIOGEOCHEMICAL ISSUES IN WETLANDS OF THE GNANGARA MOUND, SWAN COASTAL PLAIN, WESTERN AUSTRALIA

1.1 Background

The Swan Coastal Plain (SCP) stretches in area from just north of Geraldton in the north to Dunsborough in the south and is bounded by the Gingin and Darling Scarps to the east, and the Indian Ocean to the west (making it approx. 400 km long by approximately 25 km wide; Figure 1.1 shows the middle section of the SCP). It consists of Pliocene to Quaternary sediments (collectively termed 'superficial formations'; Allen, 1976) which comprise aeolian, alluvial, swamp, estuarine and shoreline sediments that were deposited on a gently seaward-sloping unconformity surface on top of Mesozoic sedimentary rocks (McArthur & Betteney, 1960). The latter rocks include the Leederville Formation (Cretaceous) and the Yarragadee Formation (Jurassic). Three major dune systems, oriented in a N-S direction, transect the SCP. The Bassendean dunes are the oldest (Pleistocene), lowest and most leached of the series. To the west of the Bassendean dune system are the siliceous Spearwood dunes which overlie limestone, and adjacent to the coast are the calcareous Quindalup dunes, the youngest unit (McArthur & Betteney, 1960).The superficial formations (i.e. sands, sandstone and limestone) support two major aquifers: the Gnangara mound north of the Swan River, and the Jandakot mound south of the river. The term 'mound' relates to the tendency of groundwater to slope away from a high central area and flow outward towards rivers or the ocean (Townley et al., 1993). The superficial aquifers are directly recharged by rainwater. The underlying mainly confined Leederville and Yarragadee formations contain vast amounts of water. Figure 1.2 shows a schematic of these groundwater resources.

Most of the wetlands on the SCP occur in inter-dunal swales and are hence also oriented in N-S direction (Figure 1.1). Although some are perched, the majority of these wetlands are hydraulically connected to the underlying superficial aquifers. Of the two superficial aquifers, the Gnangara mound is by far the more significant in terms of size

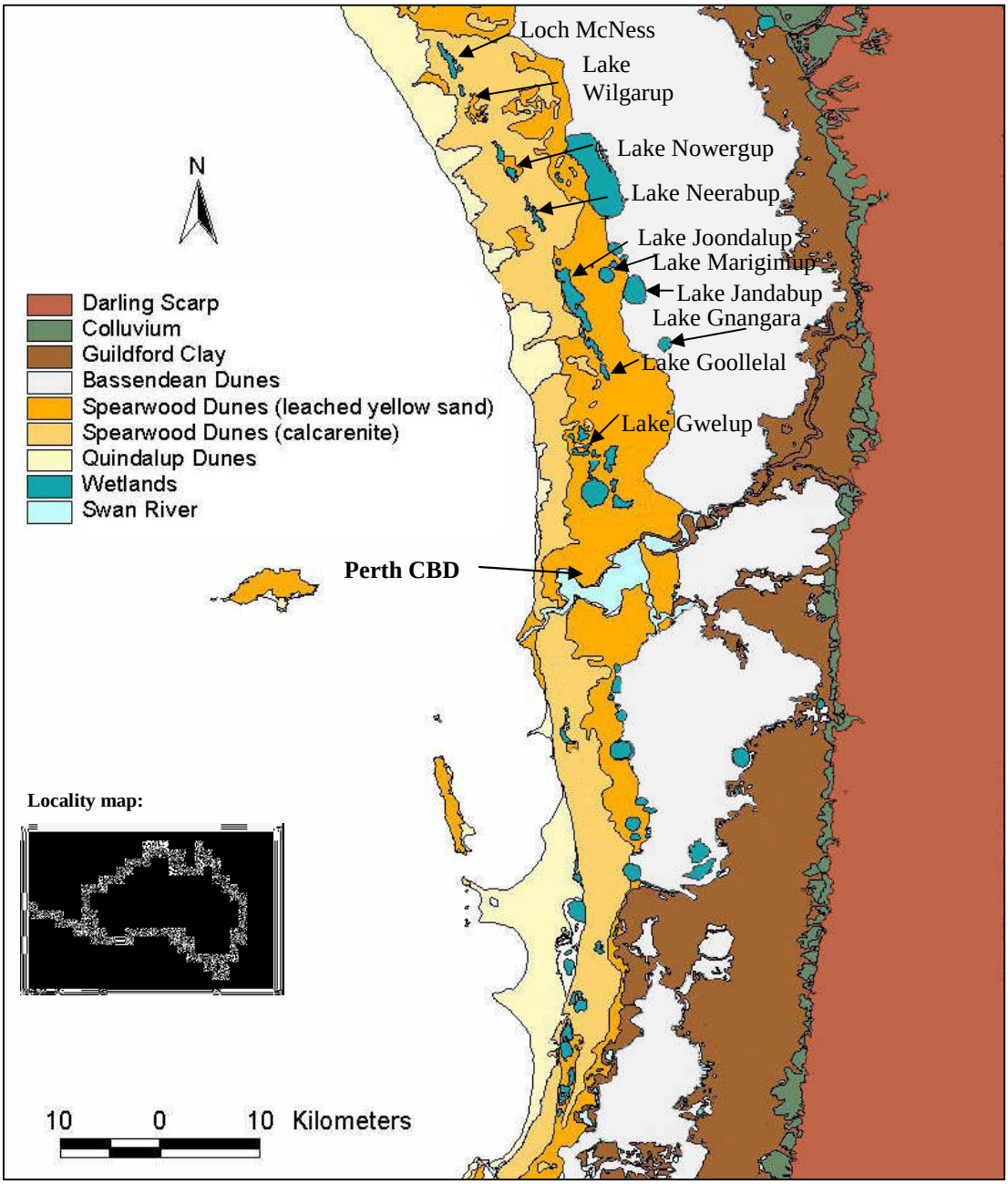


Figure 1.1: Swan Coastal Plain (middle section), Western Australia, showing generalised surface geology and wetlands**.** Wetlands referred to in this thesis are labelled.

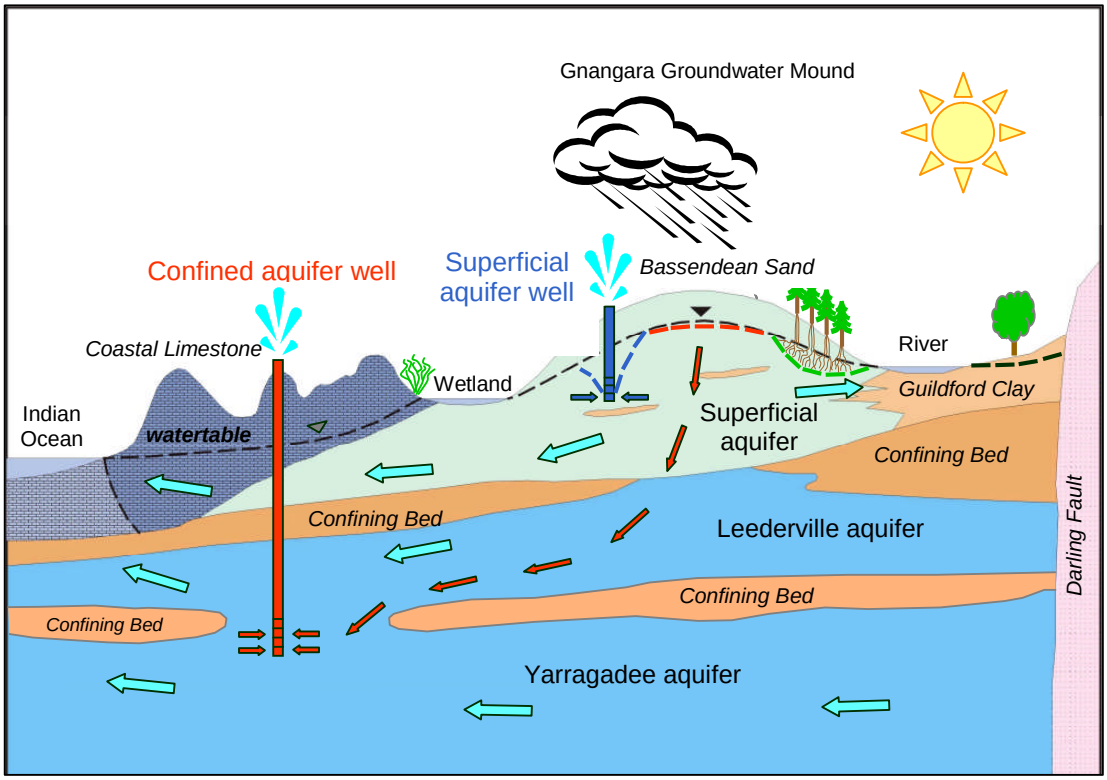


Figure 1.2: Groundwater resources of the Swan Costal Plain, Western Australia. This diagram was created from the viewpoint of providing water and is therefore not a factual representation of the hydrogeology of the Swan Coastal Plain. It does however nicely depict the inter-connectivity between the wetlands, the superficial aquifer and the underlying confined aquifers. (Courtesy of the Western Australian Department of Water).

and public water supply. It stores >20,000 GL of good quality water, with the crest of the 'mound' being 70 metres above sea level at maximum saturation (Government of Western Australia, 2003). At present it supplies up to 60% of Perth's drinking water as well as supplying irrigation for horticulture and agriculture, and for public open space and garden bores. The aquifer is also important for sustaining numerous groundwater-dependent ecosystems such as phreatophytic (groundwater-dependent) terrestrial vegetation, mound springs and caves, besides the wetlands. Perth (current population ~ 1.9 million) is a rapidly expanding metropolis which exerts ever-increasing demands on water resources. This increased demand, combined with decreasing winter rainfall, has resulted in serious aquifer depletion (nearly 600 GL since 1979), with drawdowns reported to be as much as 6 metres at the top of the mound (Department of Environment, 2005). Consequently, many of the groundwater dependent seasonal wetlands on the mound have been experiencing prolonged and more severe summer drying (Department of Environment, 2004; Knott & Storey, 2004; Clark & Horwitz, 2005; see also Figure 1.3.).

Figure 1.3: The dry lake bed of Lake Jandabup (see map in Figure 1.1 for location), March 1998, showing exposed diatomaceous sediments (foreground) and sandy sediments in the background. This lake has been artificially supplemented with groundwater from the Leederville aquifer (see Figure 1.2) since 1999 in order to prevent recurring acidification events. (Photo: B. Sommer)

The debate over whether climate change or over-extraction is the dominant force responsible for aquifer drawdown and Perth's 'water crisis' is a contentious one. To put matters into perspective, however, Figures 1.4 and 1.5 show that, whilst Perth rainfall over the past 30 years has certainly declined somewhat, total water consumption has nearly quadrupled over the same period. With Perth's population continuing to grow steadily, and projected climate trends expected to remain drier than in the immediate past (IOCI, 2002), pressures on the Gnangara mound and its dependent ecosystems can only intensify in the near future.

1.2 Drawdown and biogeochemical issues in the Gnangara mound wetlands

In Western Australia, water resource management agencies are legally required to ensure that there are no environmental impacts from groundwater extraction (the relevant legislation being outlined in Section 46 of the *Environmental Protection Act 1986 (EPA)*). As a result water level criteria have been set for each of the major wetlands on the SCP based on their ecological water requirements (EWR). The

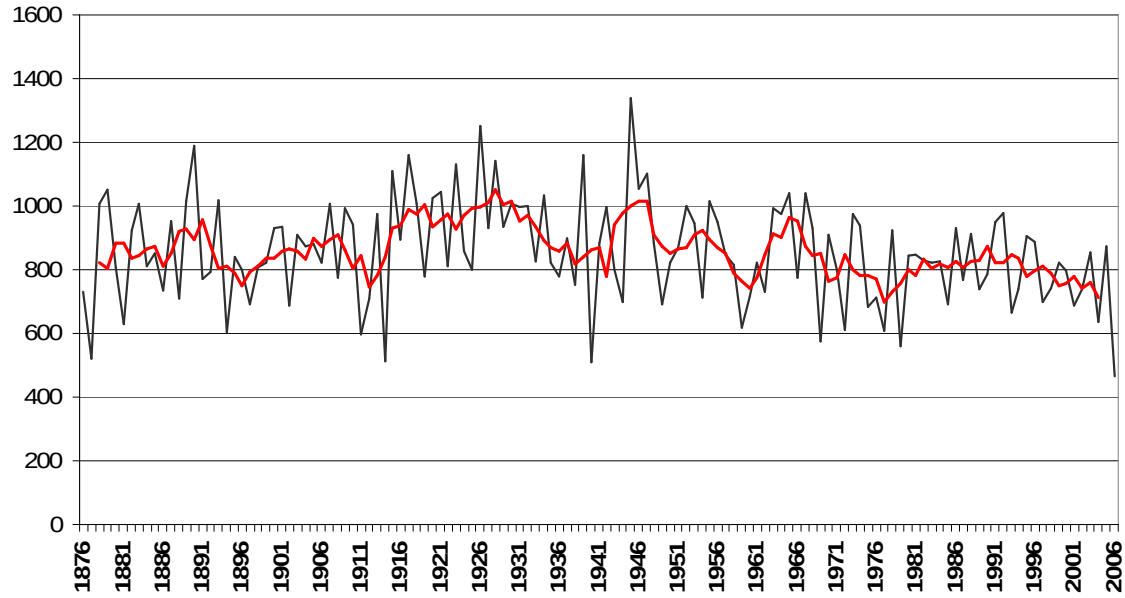


Figure 1.4: Perth Regional Office annual rainfall totals in mm 1876-2006, with 5 year moving averages. (Compiled from Bureau of Meteorology data; source: Warwick Hughes).

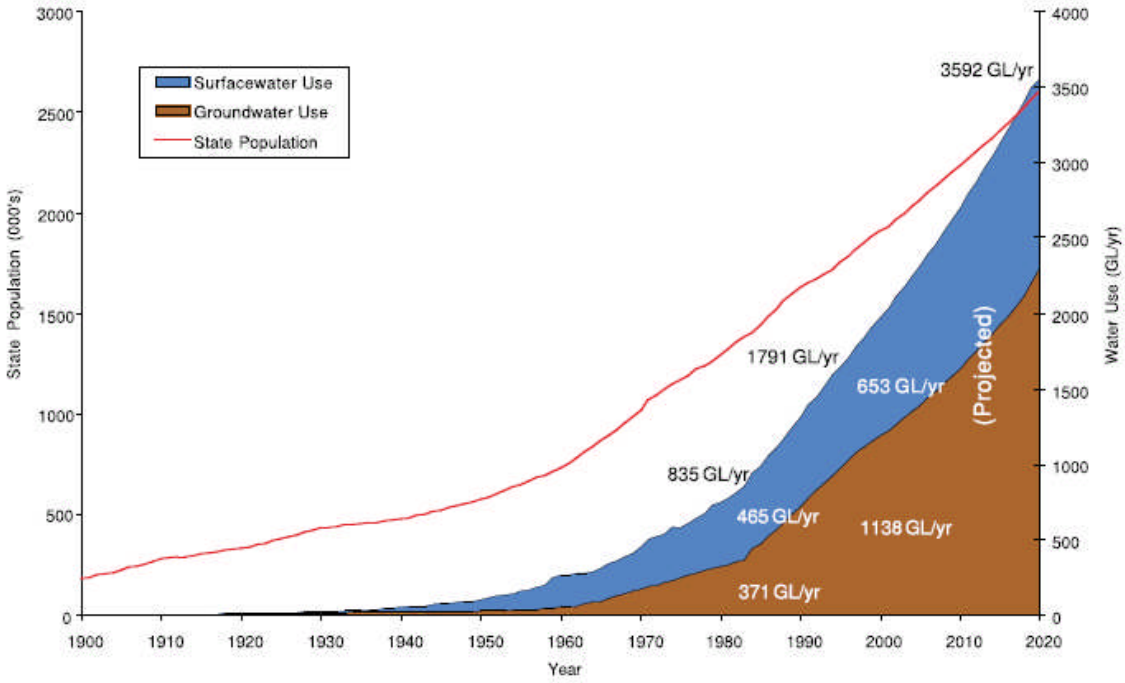


Figure 1.5: Projected water demand growth in the Perth region (Source: Government of Western Australia, 2003).

ministerial conditions further specify that regular monitoring of ground- and surface water levels, vegetation health and aquatic macroinvertebrates take place twice a year. During the past decade the incidence of breeches of the set wetland water level criteria has been increasing, and it is slowly being acknowledged that the biogeochemical impacts of these low water levels and drying may be more significant (ecologically and socially) and difficult to 'treat' than direct 'ecological impacts' *per se*. The two most common biogeochemical impacts of water table drawdown on the Gnangara mound wetlands are acidification at one extreme, and eutrophication at the other (see Figures 1.6 and 1.7). Of the two, acidification has received greater political attention because of the potential for downstream acid plumes which could be detrimental to human health. Furthermore, monitoring detected serious impacts on aquatic macroinvertebrate community structure (including local extinctions) at one of the wetlands (Lake Jandabup) following the prolonged summer drought of 1997/1998 (Sommer & Horwitz, 2001). However, eutrophication can also have serious health and ecological implications (see Chapter 2). The most publicised (locally) of these are nuisance midge (Chironomidae) swarms and unpleasant odours following drought and reinundation.

The processes involved in determining whether a wetland will acidify or become eutrophic (or both) as a result of drawdown are still poorly understood generally, but on the SCP there is an additional 'challenge'. Surface water quality of the wetlands largely reflects groundwater quality, with the Bassendean wetlands historically tending to be coloured, base-poor and slightly acidic, while wetlands on the Spearwood and Quindalup dunes tend to be richer in calcium carbonate with relatively high to very high pH. Many of the Spearwood wetlands are eutrophic due to high nutrient loads, and drying appears to exacerbate this. On the other hand, many of the monitored Bassendean wetlands also have relatively high nutrient inputs but are not eutrophic, and drying appears to bring about acidification. In fact all of the monitored Bassendean wetlands on the Gnangara mound are now acidic (Clark & Horwitz, 2005), apart from Lake Jandabup where artificial water level maintenance has restored the pH to pre-acidification levels (pre-1998). The reason for the acidification of the Bassendean wetlands is likely to be the steadily dropping groundwater table, combined with the low buffering capacity of the leached sandy sediments. In a number of instances, too, fire probably exacerbated the oxidation of the organic sediments.

Figure 1.6: Example of an acidified wetland on the Gnangara mound (Lake Gnangara, March 1998; see Figure 1.1 for location). Note the exposed organic/diatomaceous sediments. This wetland has been acidified since the mid 1970's. pH of the water column is <4, and it is not being artificially supplemented. (Photo: B. Sommer)

Figure 1.7: Instant algal bloom upon rewetting of a nutrient-enriched wetland (Lake Joondalup, summer 1998). (Photo: B. Sommer)

Although the Spearwood wetlands have also been experiencing lower water levels and extended periods of drought during the past few years none of these, until very recently, have suffered from acidification events, probably thanks to good buffering from the calcareous sediments. At the time of writing, however, there is growing concern that some of the organic-rich Spearwood wetlands on the Gnangara mound are also experiencing pH declines (e.g. Lake Wilgarup, Lake Mariginiup, Lake Neerabup; see Figure 1.1). Organic sediments (peat) are particularly susceptible to acidification upon exposure because they can contain large stores of pyrite. This is especially so for peats that have had some form of marine influence during their paleohistory (Dellwig, Boettcher, Lipinski, & Brumsack, 2002), such as those on the SCP. High sulfate input from sea water (including from seaspray and dry fallout), combined with high iron and ample organic matter from terrestrial sources favour sulfate-reducing bacterial activity, creating conditions that are very conducive to pyrite formation (Giblin & Wieder, 1992). Indeed, pyritic peaty soils are not uncommon within the Spearwood dunes (Teakle & Southern, 1937). This has recently become an issue when the drainage, excavation and stockpiling of sulfide-rich peat soils for urban development caused widespread groundwater acidity and arsenic contamination in a suburb located 5 km north of the Perth CDB, and on the otherwise well-buffered Spearwood unit (Appleyard, Wong, Willis-Jones, Angeloni, & Watkins, 2004).

All of the Spearwood wetlands labelled on the map in Figure 1.1 (plus numerous unlabelled ones) are suffering from drawdown at the present time, apart from one, Lake Goollelal (photo on front cover). A number of these are in danger of drying for the first time (at least in recent history). They have varying degrees of organic matter type and content and nutrient status, although none of the sediments of any of the wetlands have been characterised for management purposes. This makes it difficult to formulate appropriate management strategies for the individual wetlands, because the processes influencing drought-induced acidification and/or eutrophication are not understood in this particular setting.

1.3 This thesis

There are no published Australian studies that have investigated processes associated with drought-induced acidification of shallow, freshwater wetlands, nor any that have investigated the combined potential for acidification and eutrophication of organic-rich sediments (where impacts can be expected to be greatest). In fact the role of wetland sediments in drought-related aquatic processes is poorly understood, and

does not as yet form part of any wetland management plans in Western Australia. The broad aim of this research was to identify and describe the overall effects of drying and rewetting on the biogeochemistry of organic wetland sediments. Lake Goollelal (see Figure 1.1 for location), was chosen as a study site because of the organic-, nutrient- and iron-rich status of its sediments, making it ideal for a study of both drought-induced eutrophication and acidification potential. The high pyrite content of the sediments was only discovered after sediment analyses carried out as part of this research. It was not previously known (nor suspected, due to the alkaline pH of the surface water). In addition, there are no records of this lake having ever dried. It was considered to be important to use sediments with no past history of drying for the investigations in this research because drying, especially repeated drying/wetting cycles, can bring about irreversible changes (such as changes in mineralogy, changes in P partitioning etc.; see Chapter 2) in sediment properties.

The thesis is organised as stand-alone chapters, each containing an introduction and conclusion, and each addressing specific questions of this research project. Because of this layout a certain degree of repetition, especially in the introductions, was unavoidable. The main aims/questions and hypotheses are given in Table 1.1, with references to the chapters which address these. The rationales behind the formulation of the questions and hypotheses are based on the literature reviewed in Chapter 2. The methodological approach of the research as a whole is based on inferring biogeochemical processes from known relationships between measured variables as a means of improving our understanding of wetland function. The reasoning for this was a trade-off between detailed experimental work on a single attribute or variable (e.g. iron cycling) and a more holistic or 'big picture' approach. Due to the complete lack of biogeochemical information on the aquatic sediments of the system in question (i.e. the Gnangara mound) it was decided that the 'big picture' approach would be more useful and informative in the first instance. Specific areas in need of further detailed investigations will spring from this initial 'big picture' approach.

Whilst the questions and hypotheses presented in Table 1.1 sound simple enough, and many have been asked and tested previously (see Chapter 2), albeit in different settings, they have not been applied to 'truly aquatic', highly organic sediments. Yet it is in these organic systems where observed responses to hydrological change, particularly to drawdown and drought, tend to be the most severe. Although this thesis focuses on the SCP in Western Australia, many similar wetland systems occur in

other areas of the world suffering from similar water supply problems due to reduced rainfall and various anthropogenic factors (e.g. Spain, Israel, Iraq, Florida Everglades, southern Africa, and even England [Burston, 2006], just to name a few). And so therefore, the findings of this research should be beneficial beyond the geographic boundaries in which they were made.

A note on terminology: Throughout this thesis the term 'biogeochemistry', as opposed to 'geochemistry' is used. The reason for this is that the great majority of the processes discussed are in fact biologically mediated, even though no direct investigation of the biological components was made. Using the term 'geochemistry', simply because no direct biological measurements were made, would be a misrepresentation of this fact. The terms 'sediments' and 'soils' in this thesis are used in the sense of the definitions given in Semeniuk & Semeniuk (2004). In summary, *sediments* refers to 'accumulated material that either has formed wholly within the wetland (autochthonous, intrabasinal sediment, i.e., that formed inside the basin), or has been transported into the wetland (allochthonous, extrabasinal sediment, i.e., that formed outside the basin)'; and *soils* refers to 'the altered material near or at the surface of any pre-existing sediment or rock body that has been biologically, chemically, or physically modified under extant conditions' (Semeniuk & Semeniuk, 2004).

Table 1.1:

Main aims, questions and hypotheses

Aims, questions and (null-) hypotheses	Chapter
• To provide a literature review on the effects of drying and rewetting of wetland sediments. This is to serve not only as the foundation for this thesis, but also to emphasize to managers the importance of incorporating sediment-related processes into wetland management plans.	2
• To describe the sediment physical and bulk characteristics of the study site, Lake Goollelal. *Can simple sediment physical and bulk characteristics (including proxies such as elemental ratios), and with the help of univariate, bivariate and multivariate statistics, be used to infer within-wetland function, including responses to disturbances such as drought?*	3
• To investigate the biogeochemical effects (with a focus on acidification and eutrophication) of drying and rewetting of the Lake Goollelal sediments under aerobic and anaerobic conditions. *Will aeration of the sediments result in acidification if the buffering capacity is low?* H_0: Aeration of both dried/rewet and continuously wet (and previously anaerobic) sediments will result in acidification if the buffering capacity is low. Rationale: If there is not sufficient Ca(and Mg-)CO_3 in the sediments to neutralise the	4

oxidised sulfur, the sediments will acidify. *Does drying exacerbate acidification under aerated conditions?* H_0: The dried/rewet and the continuously wet (previously anaerobic) sediments will acidify to the same degree if the buffering capacity is low. Rationale: It is possible that drying, which causes physical changes in the sediments, could exacerbate acidification. One regularly sees in the literature phrases such as "….desiccation caused acidification." (e.g. Lucassen, Smolders, & Roelofs, 2002). *Will drying/rewetting cause acidification if anaerobia is quickly restored?* H_0: Drying/rewetting will not result in acidification if anaerobia is quickly restored. Rationale: If the aeration period is short, only small amounts of oxidation products will be produced, and subsequent reinstatement of anaerobia will reduce these quickly. *Will aeration decrease the amount of phosphorus released from continuously wet sediments?* H_0: Aeration of continuously wet (and previously anaerobic) sediments will result in less phosphorus release than under anaerobic conditions. Rationale: Aeration causes the oxidation of Fe^{2+} to Fe^{3+} and subsequent precipitation with orthophosphate. *Will more phosphorus be released from dried/ rewet sediment under anaerobic conditions than from sediment kept continuously wet (and anaerobic)?* H_0: There will be no difference in the amounts of phosphorus released between the dried/rewet and continuously wet sediments under anaerobic conditions. Rationale: Phosphorus release from the dried/rewet sediments may be greater than from the continuously wet ones because of the mineralization of organic phosphorus. However it could also be less if for example drying caused acidification of the sediment and much phosphorus was immobilized by aluminium. *Will aeration decrease the amount of phosphorus released from dried/rewet sediments?* H_0: Aeration of dried/rewet sediments will result in less phosphorus release than under anaerobic conditions. Rationale: Aeration causes the oxidation of Fe^{2+} to Fe^{3+} and subsequent precipitation with orthophosphate. H_0: The dried/rewet and the continuously wet (previously anaerobic) sediments will release the same amount of phosphorus less under aerated than under anaerobic conditions. Rationale: It is possible that drying-induced changes in sediment physical properties, or in the partitioning of phosphorus will result in either more or less phosphorus being bound/released.	
• To identify and compare phosphorus partitioning in dried and undried organic sediments of Lake Goollelal. • To relate phosphorus partitioning to the biogeochemical behaviour of dried/rewet and continuously wet sediments (Chapter 4). *How will drying affect the forms of phosphorus in these organic sediments?* H_0: There will be no difference in P partitioning between dried and undried sediments. Rationale: Drying is known to cause changes in phosphorus partitioning (e.g. the mineralization of phosphorus, binding properties etc.; see Chapter 2). However there are no reports on the effect of drying on phosphorus forms in highly organic, aquatic sediments.	5
• To identify and compare elemental partitioning in dried and undried organic sediments of Lake Goollelal. • To relate elemental partitioning to the biogeochemical behaviour of dried/rewet and continuously wet sediments (Chapter 4). • To investigate the effects of desiccation, as distinct from oxidation, on these organic sediments. *How will drying affect the elemental partitioning in these organic sediments?* H_0: There will be no difference in elemental partitioning between dried and undried sediments. Rationale: Drying is known to cause changes in elemental partitioning (e.g. the crystallization of oxides, binding properties etc.; see Chapter 2). However there are no reports on the effect of drying on elemental partitioning in highly organic, aquatic	6

sediments. *If an acidification response is observed in the incubation study in Chapter 4, will this be due to drying-induced changes in iron and/or sulfur partitioning, or exclusively due to oxidation?* H_0: There will be no difference in the size of the oxidisable iron and sulfur pools between the dried and undried sediments. Rationale: If the process of drying itself causes oxidation, then one might expect the size of the oxidisable pools to diminish. Iron for example might move to the amorphous (oxy-) hydroxide pool (De Groot & Van Wijck, 1993).	
• To discuss the answers to the above questions and the implications for the management of groundwater-dependent wetlands in a drying environment. • To discuss how a biogeochemical analysis of critical sediment types can characterize wetland function and response to hydrological change.	7

CHAPTER 2
A REVIEW OF THE EFFECTS OF DRYING AND REFLOODING ON WETLAND SEDIMENTS (WITH SOME NOTES ON BIOTIC AND ECOLOGICAL CONSEQUENCES)

2.1 Introduction

Alternate cycles of wetting and drying are an expected occurrence in many wetlands, particularly shallow ones. Indeed, the degree of water permanency (or 'hydroperiod') is such an intrinsic characteristic of wetlands, and an important determinant of the availability of specific habitat types, that it is a major criterion used in a number of wetland classification schemes (e.g. Cowardin, Carter, Golet, & LaRoe, 1979; Ramsar Convention Bureau, 1991; Semeniuk, 1987; Semeniuk & Semeniuk, 1997; Winning, 1996). For instance, a wetland can be permanently inundated, seasonally or intermittently inundated, or seasonally waterlogged (Semeniuk & Semeniuk, 1997). Depending on its geomorphology, however, even a permanent wetland such as a lake or a river, can dry seasonally along the edges, and many wetlands do have zones matching all four categories. As a result, the peripheries of wetlands tend to have quite different sediment characteristics than their centers. Where the sediments are saturated for sufficiently long periods on an annual basis, and the rate of biomass production is greater than its breakdown, organic matter in the form of peat will accumulate. Typically there will be a gradient from high to low organic matter content from the center of a wetland towards its edges. This, along with other sediment characteristics (many of which also are a consequence of the water regime) then determine the distribution of vegetation communities, and consequently the types of fauna living in the various habitat types.

Apart from geomorphology, climate is arguably the most important factor dictating the particular water regime of a wetland. For many decades now the natural ecological balance[*], and indeed the very existence of wetlands, has been threatened by industrialisation and the demands for land and water by an ever-increasing global human population. These threats are becoming increasingly compounded by global

[*] Definition of 'natural ecological balance' (Allaby, 1998): "A state of dynamic equilibrium within a community of organisms in which genetic, species and ecosystem diversity remain relatively stable, subject to gradual changes through natural succession".

warming and climate change which have the potential to transform the essential character of wetlands (Poff, Brinson, & Day, 2002), and lead to shifts in their geographical distribution (Bergkamp & Orlando, 1999). In essence, a warming global climate should bring about increased evaporation rates and consequently increased precipitation. However, it is predicted that regional climate changes will likely be very different from changes in the global average. In terms of hydrology, a rise in sea level could cause flooding and increased inundation of some low-lying areas (and thus increase wetland areas). On the other hand, if evaporation rates exceed precipitation soils will become drier, there will be drawdown of regional aquifers, lake levels will decline, and rivers will carry less water. When increased evaporation and a decrease in precipitation are combined with over-consumption, the effect on regional water supply can be quite dramatic. Many southern Mediterranean countries have been experiencing extreme water shortages for well over a decade now. In Israel, for example, a coastal aquifer has been drawn down so much that the water table has fallen below sea-level (Pearce, 1993). In Perth, Western Australia (population ~1.9 million) the superficial aquifer that provides up to 60% of the city's drinking water has experienced huge drawdowns in the last 30 years. The people of Perth have not only had to pay the price for its 'water crisis' through measures such as sprinkler bans and increased water rates, they have also had to pay an environmental price in terms of the degradation, and in some instances the loss, of some groundwater dependent wetlands and cave systems (see e.g. Department of Environment, 2004; Knott & Storey, 2004; Clark & Horwitz, 2005).

As indicated above, the biota of wetlands are adapted to particular water regimes, including periods of drought. Climate change, over-consumption and poor land management practices in water catchments, however, have the potential to bring about excessive and/or prolonged drying in wetlands. When this occurs, it can be expected that physical and biogeochemical processes initiated in the sediments when they dry will be more pronounced, the effects on water quality upon reflooding, more extreme, and potential recovery more difficult. Two specific problems commonly associated with drying wetland sediments are eutrophication (and associated algal blooms, malodours and nuisance insect swarms) and acidification (and associated problems such as heavy metal mobility, mosquitoes, etc.). The severity of such impacts depends on a number of factors, sediment characteristics (particularly the type and amount of organic matter present) arguably being the most important of these (McComb & Qui, 1998). Other factors are the type of drawdown (gravity or evaporative), severity of drying (proportion

of drying area, rate of drawdown, degree of dewatering, temperature and duration of drought), conditions of refilling (rate of refilling, origin of water, degree of sediment disturbance – Fabre, 1988), and exposure of sediment to a history of a specific hydrological regime (e.g. repeated drying - Mitchell & Baldwin, 1998). Apart from distributional changes of flora and fauna caused by a potentially permanent change in hydrological regime, it is mainly the changes in water quality that affect the biota of lacustrine systems. Hence, it is important to understand the geochemical processes involved when sediments dry and are reinundated.

Wetland managers in Australia have generally given little or no attention to the role of sediments in wetland ecosystems. One reason for this may be that relevant information is dispersed amongst several disciplines. This chapter contributes to the understanding of wetting-drying related processes in wetlands, particularly in ones with organic-rich sediments, firstly by drawing together the limnological, soil science and other relevant disciplines. Secondly, this chapter concludes with a simple conceptual model based on the literature that should hopefully emphasize the importance of incorporating sediment-related processes into wetland management plans, particularly in a dry country such as Australia. This literature review and the conceptual model also serve as the foundation for the following chapters in this thesis.

2.2 Methods

Initially, all books and papers relating even remotely to wetting and drying of terrestrial soils and wetland sediments already in the possession of the researcher were collated. This literature was then grouped into two broad categories: physical effects of drying on wetland sediments, and chemical and biogeochemical effects of drying on wetland sediments. The latter topic was further subdivided into the two most common problems associated with drying and rewetting of wetland sediments: drought-induced acidification and drought-induced eutrophication. In order to complete the picture, physical and biogeochemical changes were linked to biotic and ecological consequences of sediment drying. After reviewing this literature, several key words and terms emerged that were used in defining the research. A broad search strategy was used, covering several separate electronic databases, including the Australian Agriculture and Natural Resources Online, MetaQuest at Edith Cowan University (http://www.ecu.edu.au/library/metaquest) which has access to numerous online databases, Yahoo, Google and Google Scholar. Each articles' references were also searched for relevant literature. In doing this, and because of the breadth of the subject

matter, the decision was made to restrict the review to relatively recent resources (i.e. 1960 onwards), published in English, and hence primarily from western sources (unless highly relevant to the research at hand).

2.3 Physical effects of drying on wetland sediments

Drying causes a number of physical changes in soil properties, including: shrinking and cracking, sediment compaction (Bresson & Moran, 1995), the aggregation of fine particles (Scheffer, 1998; Twinch, 1987), or the breakdown of larger soil aggregates. Soulides & Allison (1961) showed that intermittent drying and wetting of soils of varying characteristics markedly decreased water-stable aggregates. However, soils with high clay or organic content experienced increased tensile strength (this is a measure of the strength of the weakest failure zones) upon drying (Kay & Dexter, 1992). This is caused by organic and inorganic cementing materials (e.g. silica, aluminosilicates, carbonates, iron and organo-sesquioxide materials). A hard impenetrable crust can develop at the surface of some wetland sediments, beneath which anoxic conditions prevail (pers. observation). Disturbance of this crust, for example by rainfall, can result in the release of odorous gases (e.g. H_2S). Grootjans, Schipper & Windt (1985) found that drying irreversibly changed peat structure which rendered the organic soils more inclined to rapid mineralization, even in wet years. This may be because drying followed by rewetting shatters soil particles and exposes new and interior surfaces to bacterial action (Bartlett & James, 1980; Birch, 1960). Grootjans et al. (1985) also found that fen peat soils became more susceptible to drying after they have dried once. This may be due to the aggregation of the soil particles; La Comber, Ward & Lynch (1997) showed that large diameter particles dried faster than smaller particles, depending on peat type. Others have observed the difficulty in rewetting dry, hydrophobic peat (Watts, Naden, & Machell, 2001; Worrall, Burt, & Shedden, 2003).

Upon rewetting, previously dried sediments may start to expand, slumping may occur, and because of the aggregation of fine particles resulting from drying, the water column may be less turbid than pre-drying (thus promoting primary production). However, drying has been shown to increase DOC concentrations (i.e. increased colour) in ground and surface waters (e.g. Homann & Grigal, 1992; Mitchell & McDonald, 1992; Tipping et al., 1999; Worrall et al., 2003; Zsolnay, Erik Baigar, Jimenez, Steinweg, & Saccomandi, 1999), and large increases in DOC concentrations in surface and groundwaters have been reported from a number of European countries (see Clark, Chapman, Adamson, & Lane, 2005; Mitchell & McDonald, 1992) in recent years. This

has been attributed to higher temperatures (due to global warming) as well as increased drying of peatlands. LaForce & Fendorf (1998) however noted that this increased DOC response was often only seen several months/years after drought events, with lower concentrations of DOC observed during the drought event. The time lag was attributed to the difficulty in rewetting dry, hydrophobic peat. Nevertheless, Mitchell & Mcdonald (1992) observed a rapid initial rise in colour (peaking after 4-6 hours) when dried peat was rewetted, followed by a gradual decline.

Bresson & Moran (1995) observed structural collapse upon rewetting ("slumping") of soils that had hard-set upon drying. Land subsidence is a common occurrence after the drainage of peat soils (Reddy, Wang, Fisher, & Newman, 1998). The drying-induced structural changes in soils and sediments, as well as changes in the position of the water table, can affect local hydrology. Compaction of bottom sediments, for example, could add resistance along the flow path between the regional groundwater flow system and the body of the lake, thus reducing the degree of inter-connection (Townley et al., 1993). Holden & Burt (2002) found that drought-induced structural change (i.e. increased macropores) in surface blanket peat layers in Britain reduced surface runoff, and increased infiltration and flow within the deeper peat layers. Drought can reverse groundwater flow patterns within peatlands (Siegel, Reeve, Glaser, & Romanowicz, 1995; Warren, Waddington, Bourbonniere, & Day, 2001). Such shifts in hydrology may considerably affect biogeochemical functions in both lacustrine (Warren et al., 2001; Winter & Rosenberry, 1998) and lotic (Dahm, Baker, Moore, & Thibault, 2003) systems.

2.4 Chemical and biogeochemical effects of drying on wetland sediments

2.4.1 Characteristics of submerged soils and sediments

The terms 'sediments' and 'soils' in this thesis are used in the sense of the definitions given in Semeniuk & Semeniuk (2004). In summary, *sediments* refers to 'accumulated material that either has formed wholly within the wetland (autochthonous, intrabasinal sediment, i.e., that formed inside the basin), or has been transported into the wetland (allochthonous, extrabasinal sediment, i.e., that formed outside the basin)'; and *soils* refers to 'the altered material near or at the surface of any pre-existing sediment or rock body that has been biologically, chemically, or physically modified under extant conditions' (Semeniuk & Semeniuk, 2004).

Chemical and biological processes in aquatic systems are difficult to separate because the majority of chemical processes are biologically mediated. Comprehensive

reviews of the chemistry of submerged soils/sediments are provided in Ponnamperuma (1972), Mitsch & Gosselink (2000) and Kirk (2004). The most significant characteristics of a submerged soil are the absence of free oxygen, and reducing conditions. The pore spaces are filled with water and oxygen diffusion into the soil is drastically limited. Any oxygen trapped in the soil is quickly consumed by soil organisms, until the soil becomes anaerobic. However, a submerged soil is not uniformly devoid of oxygen. Oxygen is usually present as a thin layer at the soil-water interface. This oxidised layer is very important ecologically, because it creates a sink for nutrients, and forms a barrier to the passage of reduced substances and certain plant nutrients into the water column (Mitsch & Gosselink, 2000). Stratification of the water body can result in the disappearance of this oxidised layer, effectively shifting the boundary of aerobic and anaerobic zones above the sediments and into the hypolimnion. However, aerobic microsites may exist in this generally anaerobic zone where aquatic macrophytes are present. Atmospheric oxygen entering the stomata on the leaves of aquatic macrophytes, together with photosynthetic oxygen, is forced into the rhizosphere (Armstrong & Armstrong, 1990). Oxygen diffuses into the root environment, or is vented from dead and broken stems, thus creating conditions where oxidation can take place. This is an easily recognisable feature because oxygen causes the precipitation of iron oxyhydroxides, resulting in reddish-brown or orange coatings (plaques) on or around roots (Ponnamperuma, 1972). The presence of oxidised rhizospheres has important consequences for the ecology of the wetland because this can interfere with the efficient uptake of nutrients (Kirk, 2003). On the other hand, potential greenhouse gases such as methane can be efficiently oxidised in these zones (Schipper & Reddy, 1996).

The reduction of submerged sediments over time proceeds roughly in the following set sequence (oxidation reactions occurring in the reverse order): $O_2 \rightarrow H_2O$, $NO_3^- \rightarrow N_2$ (gas), $Mn^{4+} \rightarrow Mn^{2+}$, $NO_3^- \rightarrow NH_4^+$, $Fe^{3+} \rightarrow Fe^{2+}$, $SO_4^{2-} \rightarrow H_2S$, organic matter $\rightarrow CH_4$. The same general sequence also applies to the vertical distribution of redox components in wetland sediments. The term ‘general sequence’ is used here because there is a significant overlap in redox potentials for different reactions (Wetzel, 2001). For example, if sulfate is reduced to sulfide and Fe^{3+} is present in the sediments, the sulfide can reduce the Fe^{3+} to Fe^{2+}, so although sulfate was reduced first, it would appear as Fe reduction occurred before sulfate reduction (Megonigal, Hines, & Visscher, 2004). Redox processes are pH dependent, and almost always microbially

mediated (Stumm & Morgan, 1996). If the sediments stay submerged for long enough on an annual basis they develop distinctive gley horizons resulting from oxidation-reduction processes (Ponnamperuma, 1972):

- a dark brown, partially oxidised horizon high in organic matter
- a mottled zone in which oxidation and reduction alternate
- a permanently reduced zone which is bluish green.

Reduction of submerged sediments is a consequence of anaerobic respiration by soil bacteria. Anaerobic respiration is generally considered to be less efficient than aerobic respiration, hence decomposition is slow, and there is a net build-up of organic matter. It is estimated that approximately 5-20% of the carbon fixed by photosynthesis is accumulated into peat in water-saturated, anaerobic conditions (Minkkinen, Vasander, Jauhiainen, Karsisto, & Laine, 1998). O'Connell, Baldwin, Robertson, & Rees (2000), however, found that rates of dissolved organic carbon (DOC) utilisation by microbiota occurred at similar rates under aerobic and anaerobic conditions, although there were clear differences in the microbial communities that developed under different oxygen availability. They postulated that the difference in the rate of breakdown of particulate organic matter under aerobic and anaerobic conditions was due to the limited growth of fungi under anaerobic conditions. The decomposition end products of anaerobic respiration are CO_2, H_2, CH_4, NH_3, NH_2, H_2S and partially humified residual organic matter (Ponnamperuma, 1972).

The primary effect of alternate wetting and drying of soils and sediments is a change in oxidation-reduction (redox) potential. Changes in redox potential invariably involve pH changes because most redox reactions consume or produce protons, and the stoichiometry is often such that redox potential is very sensitive to pH (Kirk, 2004). The physical significance of the concept of electron activity, or redox potential is, however, controversial. Thorstenson (1984) stated that, based on thermodynamic data, hydrated electrons could not exist at physically meaningful equilibrium concentrations under natural conditions, and therefore could not be measured in natural waters. Similarly, Chapelle, Haack, Adriaens, Henry, & Bradley (1996) demonstrated that H_2 concentration was more useful for identifying anoxic redox processes than E_h measurements in a polluted groundwater system. However, they further contended that H_2-based redox zone delineations are more reliable when H_2 concentrations are interpreted in the context of electron-acceptor (oxygen, nitrate, sulfate) availability and the presence of final products (Fe(II), sulfide, methane) of microbial metabolism. One

suggestion as to why redox potential is affected by pH is that Eh, measured using the platinum electrode, is actually measuring pH (D. Baldwin, pers. comm.). Ponnamperuma (1972) in his studies of tropical rice paddies stated that the overall effect of submergence was to increase the pH of acid soils and to depress the pH of sodic and calcareous soils (i.e. a convergence towards neutral), although the pattern of change is influenced by soil properties such as organic matter and iron content, as well as temperature. The increase in the pH of submerged acidic soils was due to reduction processes which generate alkalinity, and the decrease in pH of submerged calcareous and sodic soils was due to the accumulation and partial pressure of CO_2.

Ferrous iron (Fe^{2+}) is the main inorganic reductant (i.e. it loses an electron, and in the process, is oxidised) in submerged soils (although it accounts for <1% of reducing capacity, the bulk of reducing substances being organic; Ponnamperuma, 1972). Ferric iron (Fe^{3+}) is the most common oxidant (i.e. it gains an electron, and in the process, is reduced) in most soils. The reduction of Fe^{3+} results in a greater concentration of water-soluble iron, and pH increases. Cations are displaced from exchange sites, the solubility of phosphorus and silica (see below) increases, and new minerals are formed. The zone of permanent waterlogging is sometimes bluish green due to the presence of ferrous compounds. Acid soils high in organic matter and iron build up very high concentrations of soluble Fe^{2+} within 1-3 weeks of submergence; this then decreases as sulfur is reduced and sulfide minerals (e.g. FeS_2) are formed (although Ponnamperuma (1972) suggested the decreases could also be due to the precipitation of $Fe_3(OH)_8$). Roden & Edmonds (1997) confirmed that precipitation of Fe(II)-(oxy-)hydroxide-PO_4 complexes occurs in iron-rich anaerobic sediments when sulfate is lacking. These processes depend on temperature, pH, organic matter content and the crystallinity of the oxides.

Manganese is present in anoxic soil solutions as Mn^{2+}, $MnHCO_3$ and in organic complexes. The reduction of manganese in submerged soils precedes that of iron. The main transformations of manganese in submerged soils are the reduction of Mn(IV) oxides to Mn(II) oxides, an increase in the concentration of water-soluble Mn^{2+}, precipitation of manganous carbonate, and reoxidation of Mn^{2+} diffusing or moving by mass flow to oxygenated interfaces in the soil (Ponnamperuma, 1972). Acid soils high in manganese and in organic matter build up water soluble Mn^{2+} concentrations as high as 90 ppm within a week or two of submergence, then show an equally rapid decline to a fairly stable level of ~10 ppm. The reasons for the steep decline are unclear. Soils high

in manganese but low in organic matter also give high peaks but they occur later and are broad like those of Fe^{2+} at low temperatures. Alkaline soils and soils low in manganese rarely contain more than 10 ppm water soluble Mn^{2+}. Soils high in manganese (or low in organic matter) maintain positive redox potentials even 6 months after submergence. Soils low in active Mn and Fe (sandy soils) with more than 3% organic matter attain E_h values of –0.2 to –0.3 V within 2 weeks of submergence. When a flooded soil is drained, Fe(II) being more easily oxidised than Mn(II), is rapidly converted to Fe(III) oxide hydrates. These precipitates may sorb Mn^{2+} or form coprecipitates to give stains, and nodules.

The cycling of sulfur is spatially and temporally dynamic and strongly influences many biogeochemical reactions in sediments, such as the binding of phosphorus (Holmer & Storkholm, 2001). The main effect of drying and aeration on wetland sediments is the oxidation of reduced sulfur to sulfate. Upon rehydration the sulfate reacts with water to form sulfuric acid. In poorly buffered wetlands this then results in a lowering of pH (see below). However, many factors are involved in sulfur cycling such as oxygen and sulfate concentrations, temperature and organic matter availability. Hence, sulfate reduction in oligotrophic lakes is low due to limited availability of organic matter, while it may be significant in eutrophic and dystrophic lakes, where organic matter and sulfate concentrations are higher (Holmer & Storkholm, 2001). Sulfate reduction in acidic lakes can be low because of reduced microbial activity. Sulfate reducing bacteria function best in the pH range 5.5-9.0 (Ponnamperuma, 1972). Hence, while in neutral and alkaline soils extremely high concentrations of SO_4^{2-} can be reduced to zero within six weeks of submergence, acid soils show a much slower decrease, spread over several months.

Aluminium, although redox-insensitive, is important in relation to effects of wetting/drying regimes on wetland sediments because of: (1) the role of aluminium in soil and water acidification, and its toxicity, and (2) the involvement of aluminium in the phosphorus cycle. Aluminium hydroxides (e.g. gibbsite) play an important role in the formation of acidity in agricultural and submerged sediments through their complex reactions with colloidal clay particles (Boyd, 1970). Moreover, as the pH of the soil solution decreases, the solubility of aluminium hydroxide increases dramatically. The toxicity of Al varies with pH and other physico-chemical properties of water (National Water Quality Management Strategy, 2000). Al is soluble at pH values <6, and is most toxic at pH 5.2 to 5.8. Dissolved Al tends to combine with phosphates thus

immobilizing much of the phosphates in sediments and the water column (Boyd, 1970). Qui & McComb (1995) found no drying-induced increase in crystallinity in aluminium, in contrast to iron. Ulrich & Pothig (2000) have shown that as pH recovered from acidification Al precipitated only if sulfate or phosphate ions were added to the solution. They further found that phosphate elimination from solution with Al was much higher than with Fe. When Al and Fe were added together, more phosphate was bound to Al than to Fe. The authors suggested that co-precipitation of Al and phosphates could lead to the accumulation of these elements in sediments since, unlike Fe, Al can continue to immobilize phosphates even under anoxic conditions. The findings of Kopacek, Hejzlar, Borovec, Porcal, & Kotorova (2000) from a study of an acidified watershed lake in Bohemia agree with Ulrich and Poethig's (2000) study.

The concentration of silica in natural waters is usually low because of sorption by hydrous oxides of Fe and Al, as well as recombination with aluminium silicates (releasing H^+ ions in the process; Stumm & Morgan, 1996). Dissolved silica in soil solutions decrease with increase in pH up to about pH 8 (Ponnamperuma, 1972). Because of these buffering characteristics, it has been suggested by Sillen (1961, cited in Ponnamperuma, 1972) that silicate equilibria rather than the carbonate system control the pH of submerged soils. The concentration of dissolved silica in submerged soils increases slightly after flooding and then decreases gradually, and after several months of submergence the concentration may be lower than at the start (Ponnamperuma, 1972). The increase in concentration after flooding may be due to a reduction of hydrous oxides of Fe^{3+} sorbing silica, and/or action of CO_2 on aluminosilicates. The subsequent decrease may be the result of recombination with aluminosilicates, following the decrease in CO_2 partial pressure (Ponnamperuma, 1972).

2.4.2 Drought-induced acidification

The number of reports on drought-induced acidification of surface (and ground-) waters has been increasing in the last 10-15 years. Drought-induced acidification has two main causes: the re-oxidation of sulfur derived from atmospheric acid deposition or anthropogenic pollution, or the oxidation of naturally pyritic soils or sediments. Wetlands can mitigate the effects of sulfur pollution or atmospheric deposition by retaining some of the sulfur inputs through reactions with metals, thus also forming pyrite or other metal sulfides (Hughes, Reynolds, Hudson, & Freeman, 1997). In both cases therefore, acidification results from the oxidation of previously buried sulfide

minerals and proceeds according to the following chemical equations (after Singer & Stumm, 1970):

$$FeS_2+7/2O_2+H_2O\rightarrow Fe^{2+}+2SO_4^{2-}+2H^+ \quad (2.1)$$

$$Fe^{2+}+¼O_2+H^+\rightarrow Fe^{3+}+ ½H_2O \quad (2.2)$$

$$Fe^{3+}+ 3H_2O\rightarrow Fe(OH)_{3(s)}+3H^+ \quad (2.3)$$

$$FeS_2+7Fe_3(SO4)_3+8\ H_2O\rightarrow 15FeSO_4+8H_2SO_4 \quad (2.4)$$

Equation (2.4) shows the reduction of ferric iron by pyrite itself, where sulfide is again oxidised releasing acidity, along with additional ferrous iron which may re-enter the reaction cycle via equation (2.2). Ward, Sullivan, & Bush (2004) demonstrated this for highly acidic acid sulfate soil (ASS) materials, where anoxia failed to halt sulfide oxidation and acidification.

In calcareous soils and sediments, decreases in pH are buffered by dissolution of calcium carbonate:

$$CaCO_3+H^+\Leftrightarrow Ca^{2+}+HCO_3^- \quad (2.5)$$

$$HCO_3^- + H_2O\Leftrightarrow H_2CO_3 + OH^- \quad (2.6)$$

Obviously the efficiency of this buffering effect against sulfide oxidation will depend on the amount of protons released and the amount of bicarbonate ions that can be produced. For instance, Lucassen et al. (2002) found that desiccation led to severe acidification of a mire in the Netherlands when the sediment S: (Ca+Mg) ratio exceeded 2:3. The pH-buffering capacity of a soil or sediment will potentially decrease as $CaCO_3$ dissolves because Ca^{2+} ions can be washed down-stream or lost through groundwater flow (van den Berg & Loch, 2000). As highlighted by the above equations, it is the oxidation of the sediment, and resulting buffering responses, that determine whether a sediment or water body will acidify or not. They give no indication as to how drying *per se* affects these processes.

In Canada, Aherne, Larssen, Dillon, & Cosby (2004) and others noted sulfate retention in lakes in forested catchments during non-drought years, and re-oxidation of previously stored (reduced) sulfur in drought years. This process is being blamed for the lack of recovery of some boreal wetlands from acidification in spite of greatly reduced sulfur emissions (Schindler, 1998). In the Netherlands, some mires have become more sensitive to drought because groundwater that either naturally feeds them, or is used to artificially replenish them, has been polluted with non-airborne sulfur (Lamers, Vanroozendaal, & Roelofs, 1998; Lucassen et al., 2002). Lamers et al. (1998) found that dried experimental cores from a mesotrophic, peaty wet meadow to which SO_4^{2-} was

added showed significant drops in pH, while the pH of control cores dropped only slightly. Upon rehydration the pH of the SO_4^{2-} -treated cores dropped further, while that of the controls did not. Waterlogging then restored the pH values of all of the cores to pre-desiccation values after about 4 weeks. This recovery was probably attributable to the original high alkalinity and acid neutralising capacity (ANC) of the soils. In a similar experiment on intact rich fen soils from Belgium, Van Haesebroeck, Boeye, Verhagen, & Verheyen (1997) also noted the reversibility of drought-induced acidification. In this case also, the groundwater was base-rich. These authors were assessing whether reduced flow of base-rich groundwater into the fens (due to climate change) would lead to acidification and threaten the rare vegetation assemblages that grow there. Carvalho & Moss (1999) also noted the extreme sensitivity of an acidic lake in lowland U.K. to drought due to negligible groundwater inputs. On the Swan Coastal Plain, Western Australia, a severe summer drought in 1998 resulted in the acidification of a poorly buffered, seasonal wetland (with considerable ecological consequences; Sommer & Horwitz, 2001). In this case, pumping of (not particularly base-rich) groundwater to maintain water levels in summer was successful at restoring the pH to pre-acidification levels after two years (Chapman & Horwitz, 2001).

Another issue is the downstream transport of SO_4^{2-} from wetlands during drought conditions. This is primarily related to the impact of drought on hydrologic controls such as residence time, water table position, hydrological pathways and sediment anoxia (Warren et al., 2001). Several studies have documented a shift from SO_4^{2-} retention to export from wetlands following summer drought (e.g. Bayley, Behr, & Kelly, 1986; Devito & Hill, 1999; Hughes et al., 1997; Lazerte, 1993; Warren et al., 2001). Apart from the potential damage this can do to receiving environments, the concomitant export of base cations leaves these wetlands much more vulnerable to acidification. Lazerte (1993) suggests this is because the cation exchange sites of the wetland will become increasingly saturated with protons and aluminium ions. On the other hand, Comfort, Dick, & Baham (1991) determined that the SO_4^{2-} - sorption capacity of air-dried soils was substantially higher (320%) than that of field-moist soils. This suggests that potentially less SO_4^{2-} would be mobilised following drought. However, soil properties such as organic matter content are likely to significantly influence SO_4^{2-} behaviour in response to drying, but research findings are not consistent. Some researchers have found positive correlations between SO_4^{2-} adsorption and organic matter, and others negative ones (see Edwards, 1998). Perhaps of even greater concern, Tipping, Smith, Lawlor, Hughes, & Stevens (2003) experimentally

demonstrated the release of metals from industrially polluted peatlands in northern England and Scotland due to drought-induced acidification. Thus drying peaty wetlands have the potential to release years worth of stored pollutants.

Drought-induced acidification (just like non-drought-induced acidification) also has the potential to decrease dissolved organic carbon (DOC), i.e. colour, in the water column thus undesirably affecting wetland organisms through increased UV-B penetration, or favouring the proliferation of algae (Bothwell, Sherbot, & Pollock, 1994; Schindler & Curtis, 1997; Sommer & Horwitz, 2001; Yan, Keller, Scully, Lean, & Dillon, 1996). This is because acidification (i.e. a decrease in pH and an increase in ionic strength) reduces the solubility of DOC. DOC is important in chelation, flocculation and changes in mobility of trace metals and other chemicals (Schindler, Curtis, Jefferson, Parker, & Stainton, 1996). Moreover, drought-induced acidification has been reported to reduce the amount of DOC that is transported from peatlands to rivers and the ocean, thus depriving these ecosystems of an important energy source (Clark et al., 2005).

Although as yet not reported for wetland sediments, drought conditions have also caused the acidification of agricultural soils due to nitrification and the production of nitric acid related to excessive use of fertilizers (see e.g. Paul, Black, & Conyers, 1999). More than 15 years ago Kelly, Rudd, & Schindler (1990) voiced concerns about the potential for lake acidification (although not drought-related) resulting from increased nitrogen loading from the atmosphere. Although much research has been carried out on the impact of drying-wetting cycles on nitrogen cycling (see below), the role that elevated N concentrations plays in drought-induced acidification is not well understood. Given that N can exist in seven oxidation states, it can be assumed that the processes involved are much more complex than acidification from H_2SO_4. It is possible for example that the presence of high concentrations of nitrate would exacerbate acidification (and/or prevent recovery) caused by the oxidation of pyrite because NO_3^- has the ability to oxidise reduced sulfur in the absence of oxygen (Golterman, 1993; see also discussion under Section 2.4.3.3). Scientists are becoming increasingly concerned about the potential impact of increased atmospheric nitrogen deposition on world biodiversity (Phoenix et al., 2006). Given that wetlands play an important role in the retention or otherwise of N inputs (Saunders & Kalff, 2001), and given the likelihood of raised temperatures in the near future, there is an obvious need to

understand the interrelationship between elevated N concentration, drought and acidification of wetlands.

2.4.3 Drought-induced eutrophication

2.4.3.1 Carbon cycling

As a general rule, drying increases the solubility of organic matter (OM) and increases the rate of decomposition. The increase in the solubility of organic matter is due to the physical shattering of soil particles, as mentioned above, and the increased rate of decomposition is due to the greater availability of lower weight molecular OM, but also to the greater availability of oxygen in the dried sediment and oxygenated water. Drying is furthermore thought to 'switch-on' the microbial extracellular enzyme phenol oxidase, increasing organic matter decomposition. Once this enzyme is 'switched-on' decomposition remains higher even after reflooding (Freeman et al., 1997; Freeman, Osstle, & Kang, 2001). In terms of leaf litter, anaerobic conditions and cooler temperatures will result in slower decomposition, than if the litter were in shallower, warmer and oxygenated water (Wetzel, 2001). Leaf litterbag studies in aquatic and semi-aquatic environments, however, have come up with mixed conclusions on the relationship between the extent of leaf litter decay and the frequency and duration of flooding (see e.g. Ryder & Horwitz, 1995; Taylor & Parkinson, 1988; van der Valk, Rhymer, & Maurkin, 1991). Likewise, peat carbon stores have been found to either decrease or increase after drainage, depending on the nutrient status and climatic conditions (Minkkinen et al., 1998). Several researchers have observed marked increases in respiration in air-dried soils that had been rewetted, as evidenced by a flush of CO_2 production (Birch, 1958; Fierer & Schimel, 2003; Soulides & Allison, 1961). Fierer & Schimel (2003) studied the effects of a single drying and rewetting event on soil C pools, and suggested that the CO_2 pulse was generated entirely from the mineralization of microbial biomass. Others have suggested that a combination of biomass C (i.e. microbes) and non-biomass soil OM-C contributed to the rewetting CO_2 pulse (see Fierer & Schimel, 2003). Van Schreven (1967), however, found that whilst the first drying and rewetting resulted in increased CO_2, repeated drying and rewetting depressed the decomposition of lucerne meal.

Laine et al. (1996) and others suggested that water-level drawdown will increase emissions of CO_2 and N_2O, whereas emissions of CH_4 would decrease from northern peatlands. These are all greenhouse gases and a change in their balance (the 'radiative forcing factor') caused by drainage would either positively or negatively affect the

greenhouse effect. Contrary to some predictions, Laine et al. (1996) proposed that drying arising from climate change would in fact decrease the radiative forcing of northern peatlands. This is because of decreased CH_4 emissions, fairly small changes in the peat carbon storage and increased tree-stand biomass storage. Whilst the production of CH_4, and indeed also of H_2S decrease during drought and oxygenated conditions, the increased mineralization rate (and associated greater availability of not only C, but also N and P) in re-saturated sediments is conducive to the establishment of anaerobic conditions and potentially higher production and emission of these gases (Crozier, Devai, & DeLaune, 1995). Even under only moderately reducing conditions Boon, Mitchell, & Lee (1997) found that ephemerally inundated floodplain wetlands in eastern Australia emitted significant amounts of methane, especially over the summer months. They attributed this to the survival and rapid reactivation of methanogenic archaea after prolonged drying of wetland sediments. It appears that the jury is still out on this issue, however, the emerging generalization is that a warming climate will result in peatlands becoming net carbon sources, rather than sinks (e.g. Funk, Pullman, Peterson, Crill, & Billings, 1994; Moore, 2002). This is all the more probable where dry organic soils become more susceptible to wildfire (Horwitz, Judd, & Sommer, 2003; Horwitz, Pemberton, & Ryder, 1999; Schindler, 1998).

In conclusion, drought-induced changes in carbon cycling have three consequences for the eutrophication of wetlands. Firstly, the increased availability of low weight (i.e. more easily degradable) OM, higher rates of decomposition which releases other nutrients (mainly N and P), and higher atmospheric CO_2 concentrations, CO_2 being the best 'fertilizer' of them all.

2.4.3.2 Phosphorus cycling

In general, phosphorus (P) availability in flooded soils tends to be high, although this depends on soil properties (Ponnamperuma, 1972). In non-calcareous soils (and this would not be expected to differ much from non-calcareous aquatic sediments) a reducing environment resulting from flooding results in an increase in soluble Fe^{2+} and concomitant liberation of sorbed orthophosphate (Szilas, Borgaard, Hansen, & Rauer, 1998). In calcareous soils the solubility of P is largely regulated by the solubility of hydroxylapatite (Stumm & Morgan, 1996). An additional fact that needs to be considered is that up to 60% of water-soluble P may be organic (Ponnamperuma, 1972). Drying and reflooding of wetland sediments, particularly organic ones, often results in an increase of P concentration in the water column (Lucassen, Smolders, & Roelofs,

2005; Qui & McComb, 1994, 1995; Szilas et al., 1998; Twinch, 1987; Van Haesebroeck et al., 1997), although the opposite has also been reported (Barrow & Shaw, 1980; Haynes & Swift, 1985; Jacoby, Lynch, Welch, & Perkins, 1982; Sommer and Horwitz, 2001). Drying-induced increases in, not only P but also other nutrients such as nitrogen, is thought to originate mainly from the breakdown of organic matter and the death of microbial biomass, and the subsequent stimulation of microbial activity (Crozier et al., 1995; Fabre, 1988; Fierer & Schimel, 2003, Mitchell & Baldwin,, 1998; Qui & McComb, 1995; Soulides & Allison, 1961; Sparling & Ross, 1988; Sparling, Whale, & Ramsay, 1985). Drying induced increase in iron crystallinity (Lijklema, 1980) has also been implicated in reductions in P binding capacity, and hence P availability (Baldwin, 1996a; McLaughlin, Ryden, & Syers, 1981; Qui & McComb, 2002). Twinch (1987) found that whilst air-drying of sediments from a hyper-eutrophic reservoir resulted in reduced bio-availability of P, the dried sediments showed a greater propensity to release P, the phosphate equilibrium concentration was increased, and the phosphate buffer capacity was diminished. Baldwin (1996a) found that sediments of a eutrophic dam that had been desiccated/oxidised had a substantially lower affinity for P than those of submerged sediments. Mitchell & Baldwin (1998) later processed sediment slurries from different hydric zones of the same dam and found that sediments from exposed sites released less P than those from the permanently inundated zone. They proposed that this was caused by carbon limitation (resulting from drying) which seriously affected bacterial community structure, as well as ageing of minerals (i.e. increased crystallization) with which P is associated. Qui & McComb (1994) found that re-wet air-dried sediments from a Western Australian eutrophic lake released P under both anaerobic and aerated conditions (although a definitive reason for the aerobic release was not established).

Decreased concentration of phosphate in the overlying water of previously dried sediments has been attributed to the direct effect of drying/oxidation, as well as to the indirect effect of lowered pH (see Kopacek et al., 2000), on the sediment binding sites (Phillips & Greenway, 1998, and others reviewed in McComb and Qui, 1998, and in Baldwin & Mitchell, 2000). Barrow & Shaw (1980) suggested that drying may decrease the degree of hydration of iron hydroxide gels thus increasing their surface area (and hence P sorption capacity). Phosphates associated with iron and aluminium predominate in acid soils and sediments, while calcium phosphates predominated in neutral and alkaline soils (Ponnamperuma, 1972). Iron and aluminium phosphates release phosphate as pH increases while calcium phosphates liberate phosphate as pH decreases (Stumm

& Morgan, 1996). Where drying results in depressed pH, the inactivation of P by Al is a likely consequence (Kopacek et al., 2000). When sulfidic sediments are exposed to air, iron sulfides present in the anoxic sediments may rapidly oxidise to amorphous ferric oxyhydroxides (De Groot & Van Wijck, 1993). The low pH (4-6) and the large surface area of these oxides means the rewetted sediments will have a very high affinity for P. Under these circumstances, the subsequent release of P, even under anaerobic conditions, will be reduced (Lovley, 1987).

The interplay between P, Fe and S is such that sulfate reduction and concomitant sulfide production leads to reduction of Fe-PO_4 complexes, and as a result, orthophosphate is released (see e.g. Caraco, Cole, & Likens, 1993). These reactions are primarily microbially driven, and it has been suggested that the reason P release can occur even after extensive drying of such sediments, is that repeated wetting/drying cycles select for bacteria that are tolerant to periods of desiccation and/or oxidation (Baldwin, Mitchell, & Rees, 2000). Roden & Edmonds (1997) demonstrated that the magnitude of orthophosphate released from Fe(III)-PO_4 complexes under anaerobic conditions is much greater in the presence of sulfate. Where sulfate was lacking in iron-rich sediments, comparatively small amounts of PO_4^{3-} were mobilised via microbial Fe(III) reduction because reduced non-sulfidic Fe(II) sorbed PO_4^{3-}, and subsequently precipitated as Fe(II)-PO_4 minerals (e.g. $Fe_3(PO_4)_2$ or Fe(II)-hydroxide-PO_4 complexes). Where abundant sulfate was present, though, sulfate reduction released substantial amounts of PO_4^{3-} (up to 100% of the initial solid-phase PO_4^{3-}). This release was directly correlated with bacterial sulfate reduction and sulfide mineral formation.

If much of the P released were from the death of microbes and the breakdown of OM though, one might expect P to be released without microbial mediation. Re-wetting of formerly drained areas has become common wetland restoration practice in a number of European countries (e.g. Lamers, Tomassen, & Roelofs, 1998; Lamers, Vanroozendaal et al., 1998; Lucassen et al., 2005; Venterink, Davidsson, Kiehl, & Leonardson, 2002). Often the recharge water is sulfate-enriched, which has the potential to affect P-release, as described above. However, Venterink et al. (2002) found that whilst the extractable P pool in dried and re-wetted soil cores from a wetland in Sweden increased, re-wetting with sulfate-enriched water had no further effect on nutrient release. Lucassen et al. (2005) found that the effect of temporary desiccation of sulfur-rich fens in the Netherlands on P mobilization and immobilization depended on the sediment Fe and P pools, in combination with sediment buffer capacity. They

discovered that desiccation and reinundation at sites with a relatively large (groundwater-derived) reduced Fe pool (as FeS_x) led to a long-term reduction in P-release because of the oxidation and release of Fe with which phosphate subsequently precipitated. Conversely at sites lacking such a pool (because of the lack of groundwater input and artificial water level maintenance with sulfate-rich water), desiccation led to severe eutrophication. Szilas et al. (1998) further determined that the P saturation (i.e. the amount of oxalate-extractable P relative to oxalate-extractable Fe and Al) was an important determinant of the amount of phosphate released from moderately acid reflooded, formerly reclaimed agricultural soils in Denmark. When the phosphate saturation status is high, more phosphate can be expected to be released under anaerobic conditions. In the Everglades, Florida, Pant & Reddy (2001) demonstrated the importance of the severity of drawdown in terms of P release. A ≤30 day drawdown not only reduced P flux to the water column, but also increased the humification and microbial immobilization of P, while excessive drawdown of 60 days triggered the release of P into the water column.

2.4.3.3 Nitrogen cycling

Nitrogen transformations in wetland sediments are at least as complex as P transformations, and are also strongly dependent on redox potential and pH. In contrast to P, where drying and rewetting can result in either more or less available P in the water column compared to continuously wet sediment, most of the literature (Birch, 1964; Qui & McComb, 1996; Van Schreven, 1967; Venterink et al., 2002 and others reviewed in McComb and Qui, 1998 and in Baldwin & Mitchell, 2000) reports an increase in available N (at least in the short term). As with P, the increases in available N have generally been attributed to the death of microbes (e.g. Bottner, 1985; Fierer & Schimel, 2002; Sparling & Ross, 1988) and increased mineralization of organic matter, the amount of N mineralized being directly related to the amount of organic matter present (Davidsson & Stahl, 2000; Grootjans et al., 1985; Hacin, Cop, & Mahne, 2001; Phillips & Greenway, 1998). When organic matter breaks down, organic nitrogen is released. This is then further decomposed by bacteria to ammonia, and then to ammonium:

$$\underset{\text{(urea)}}{NH_2CONH_2} + H_2O \rightarrow 2NH_3 + CO_2 \qquad (2.7)$$

$$NH_3 + H_2O \rightarrow NH_4^+ + OH^- \qquad (2.8)$$

If the pH is sufficiently high, NH_3 can be lost to the atmosphere via volatilization (Wetzel, 2001). Increased N mineralization results in an accumulation of ammonium in the sediments during drying, and when these are rewetted ammonium is released into the overlying water. Qui & McComb (1996) and others found that in oxygenated water, this flush of ammonium stimulated nitrification. Nitrification proceeds according to the following reaction (numerous intermediate reactions not shown):

$$NH_4^+ + 2O_2 \rightarrow NO_3^- + H_2O + 2H^+ \qquad (2.9)$$

Nitrification then stimulated denitrification in the sediments, which in turn may ultimately lead to the loss of N (as N_2 gas) from the system:

$$NO_3^- \rightarrow NO_2^- \rightarrow N_2O \rightarrow N_2 \qquad (2.10)$$

Ponnamperuma (1972) states that alternate wetting and drying increases denitrification loss, while continuous submergence minimizes this, and may even lead to accumulation of N in the sediments. Hence, Davidsson & Leonardson (1997) recommended that, in order to depress N_2O production and emission to the atmosphere, wetlands should be kept continuously waterlogged. Alternatively, McComb and Qui (1998) suggested that drying and reflooding of organic-rich sediments offers potential for nitrogen removal and thus helps control eutrophication in wetlands. This latter strategy may backfire however if drying results in increased P release, as mentioned above, especially if P, and not N is the limiting nutrient.

At Lake Jandabup, a seasonal wetland on the Swan Coastal Plain, Western Australia, enormous amounts of ammonium were released into the water column in response to an extended summer drought (Sommer and Horwitz, 2001). However, this failed to stimulate nitrification. Since the drought resulted in acidification of the wetland, Sommer and Horwitz (2001) suggested that the increase in ammonium was probably the result of H^+ ions replacing NH_4^+ ions on the sediment exchange sites. Nitrification was probably inhibited because of the effects of low pH on nitrifying bacteria. Subsequent recovery of pH resulted in a decrease in NH_4^+ concentration to pre-acidification levels (Chapman and Horwitz, 2001). Lucassen, Smolders, van der Salm, & Roelofs (2004) found that drying and rewetting of sediments receiving high groundwater nitrate inputs contained no oxidisable FeS_x, contrary to nitrate-poor sites. Laboratory tests confirmed that NO_3^- additions prevented the reduction of Fe or SO_4^{2-} under reduced conditions. Moreover, Golterman (1993) suggested that FeS could be

oxidised by NO_3^-. They demonstrated this by adding FeS to sediments and noting that this increased denitrification markedly. In Lucassen et al.'s (2004) case, reduction of Fe and SO_4^{2-} (and concomitant release of PO_4^{3-} and associated eutrophication) upon rewetting was inhibited, confirming that NO_3^- is a more favourable electron acceptor than either Fe or SO_4^{2-}. Drought-induced oxidation of FeS_x appears to not only increase the sediments capacity to sorb phosphate, it also appears to reduce the sediment's denitrification potential because of the lower availability of FeS_x (Golterman, 1993). One might conclude then, that drought-induced increase in nitrification would, at least to some extent, buffer PO_4^{3-} release by preventing the dissolution of Fe- PO_4^{3-} complexes and/or re-oxidising any FeS_x formed.

As one of the exceptions to the general rule, Mitchell & Baldwin (1999) reported that there was no flush of mineral N upon rewetting, and none of the nitrogen cycle processes were notably affected by desiccation in the sediments of a reservoir. More recently, Baldwin, Rees, Mitchell, & Watson (2005) noted that after ~3 months of *in situ* drying of stream sediments, upon re-wetting, the sediments immediately produced pulses of ammonia, nitrate and, to a substantially lesser extent, urea. However, although some differences were observed between nitrogen dynamics before and after drying, a causal linkage could not be established. There are obviously differences in the drying-rewetting response of nitrogen cycling in *in situ* experiments, compared to laboratory experiments where sediments may have been exposed to exaggerated treatments (e.g. grinding and excessive drying) not normally encountered in the field (see e.g. Groffman & Tiedje, 1988). Hydrological issues must also be taken into consideration. Where lakes subject to drying receive riverine inputs, for instance, Scholz, Gawne, Ebner, & Ellis (2002) stated that post-flood nutrient pulses are the net result of both riverine inputs and sediment releases, and that the relative significance of either may be influenced by regulation. A corollary would be that nutrient pulses after re-wetting of groundwater-fed wetlands (such as those on the Swan Coastal Plain) would also be the net result of both groundwater input and sediment release, and that either of these would be influenced by the amount of groundwater extracted.

2.5 Biotic and ecological consequences of sediment drying

Curiously there appears to be more research on the biotic and ecological consequences of drought in riverine, than in lacustrine systems. For example, of the 11 papers arising from a symposium 'The Role of Drought in the Ecology of Aquatic Systems' held in Australia in 2001, and published in a special edition of *Freshwater*

Biology (Vol. 48(7)), 2 were general, 8 dealt with lotic systems, and 1 dealt with wetlands along the reaches of the Murray River. Perhaps, this is because of the potential impacts of river regulation, and in Eastern Australia large rivers such as the Murray-Darling system are very important with regards to public water supply in the region (and hence attract more research funding). Apart from the issue of hydrological disconnectivity which e.g. prevents fish and other aquatic fauna from moving into certain reaches of the river, the effect of drought on aquatic biota can be expected to be similar in both lotic and lentic systems. For instance, both animals and plants can become adapted to, and can recover from drought by having drought-resistant eggs or seedbanks (Brock, Nielsen, Shiel, Green, & Langley, 2003). Some plants have flexible life-cycles (i.e. different growth forms) which enables them to survive in both temporary or permanent water (Brock, 1991). Low water levels and periodic drought encourages macrophyte regeneration from buried seeds, and in fact many aquatic macrophytes thrive best under fluctuating water levels (Keddy & Reznicek, 1985).

Nevertheless, in the medium to long term, a change to a drier hydrological regime will result in the shrinkage of wetland area, as the more water dependent plants move downslope, while the outer boundaries are taken over by terrestrial plants (Froend, Farrell, Wilkins, Wilson, & McComb, 1993). Ultimately, this can result in the loss of the wetland, and a changeover to a terrestrial system. As mentioned in the introduction, the hydrologic regime has profound effects on the reproduction, growth and distribution of aquatic plants (Boon, Virtue, & Nichols, 1996). This can be exacerbated by drought-induced changes in nutrient availability. For instance Grootjans et al. (1985) observed increased yield of vegetation, expansion of nitrophilous herbs and a decline in species richness as a result of increased nitrogen availability resulting from drought in wet meadows in the Netherlands. Drying-induced changes in vegetation pattern can in turn themselves affect nutrient dynamics (Serrano, Calzada-Bujak, & Toja, 2003). Competition can be a significant constraint on the successful re-establishment of wetland vegetation (Budelsky & Galatowitsch, 2000). In a small reservoir in Côte-d'Ivoire Thomas, Cecchi, Corbin, & Lemoalle (2000) observed a progressive stranding of macrophytes resulting from a steady decline in water level, until their total disappearance. The competition for light and nutrients having been removed, the reservoir shifted from being macrophyte-dominated to being phytoplankton-dominated during the same period. A wetting-drying regime can prevent the build-up and development of organic sediments in wetlands (Day Jr., 1993; Minkkinen et al., 1998; Nicholson & Vitt, 1994), and therefore the redox environment

at the sediment-water interphase. This in turn will also influence the type of vegetation growing there. Harding (1992) neatly summarised the processes of change resulting in a degradation of the vegetation community in an English fen due to groundwater abstraction: alteration of competitive balance of the community dominants; change in environmental conditions required by individual species; increases in site fertility; increase in scrub cover on the fen; and a change from groundwater to rain-fed hydrology.

Aquatic plants affect the introduction of oxygen and carbon substrates into sediments, and hence a change in their distribution will tend to impact on microbes (Boon et al., 1996), as well as nutrient availability (Serrano et al., 2003). Boon et al. (1996) found significant differences in the microbiological characteristics of permanently inundated and seasonal wetlands in eastern Australia. They advocated that hydrological regime might not only affect microbial consortia directly (as in the case of wetting and drying in ephemeral wetlands), but also indirectly by means of an influence on the distribution of aquatic plants. There is also some indication that plants and microbes may compete for soil amino acids in response to climatic disturbances such as dry-rewet or freeze-thaw events (Lipson & Monson, 1998).

The distribution of aquatic vegetation and available habitat types determine the distribution and abundance of macroinvertebrates. It can be reasoned that wetlands with permanently, as well as seasonally inundated zones will support a wide range of vegetation hydrotypes. This diversity in habitat types will necessarily also support a rich aquatic macroinvertebrate fauna (assuming good water quality). The presence of different hydrozones would also provide refuges for aquatic fauna in times of drought that would not be available in the more shallow, seasonal wetlands (that regularly completely dry). Bataille & Baldassarre (1993) found that after drought macroinvertebrates were abundant and widely distributed in three Prairie potholes of differing water permanency. In an irregularly flooded salt marsh Robert Jr. & Matta (1984) observed that the most severely dried sites were recolonised quickest by prey species. They suggested that this was because drying eliminated predator species. In desert streams subjected to drying and flooding invertebrate persistence appears to be due largely to their ability to rapidly recolonise disturbed sites (Stanley, Buschman, Boulton, Grimm, & Fisher, 1994). Recovery after drought in streams is rapid by macroinvertebrates that possess strategies to survive drying or are highly mobile, but

other taxa take longer to recolonise depending on the timing, intensity, and duration of the dry phase (Boulton, 2003; Wood & Petts, 1999).

However, where drying and reflooding result in significant changes in water chemistry, macroinvertebrate as well as microbial assemblages necessarily change. Eutrophication causes the proliferation of algal blooms, unsightly algal scums, and possible cyanobacterial poisoning of waterfowl. The non-vegetative propagules ('akinetes') of many cyanobacteria can tolerate the air-dried state for prolonged periods (Potts, 1999; Yamamoto, 1975). Low oxygen levels eliminate much of the invertebrate fauna which becomes dominated by a few resistant species such as larval non-biting midges (Chironomidae) and aquatic worms (Oligochaeta) (Davis & Christidis, 1997). Swarms of emerged midges are a constant source of nuisance in residential areas adjacent to wetlands in Perth (Western Australia). Low water levels and sediment desiccation exposes decaying organic matter and anaerobic bacteria to air, producing malodours. Low oxygen concentration and elevated temperature also result in conditions favourable to the growth of the bacterium *Clostridium botulinum*, and subsequent outbreaks of botulism among waterfowl (Mooij et al., 2005). Such conditions may also pose health risks to humans (and their pets) if they come in contact with this water.

It is universally accepted that acidification, whether drought-induced or otherwise, can have serious effects on the biological productivity of aquatic ecosystems. Changes in aquatic plant (Crowder, 1991) and algal (Faulkenham & Hall, 2003; Findlay, Hecky et al., 1999; Findlay, Kasian, Turner, & Stainton, 1999) communities have been observed under long-term acidity. Large-scale kills of fish, crustaceans and oysters have occurred in areas where sulfuric acid from oxidised acid sulfate soils has washed into waterways (Sammut, Melville, & Fraser, 1995). Acidified waters tend to have lower macroinvertebrate richness and disrupted trophic structure (Dangles & Guerold, 1999; Rundle & Attrill, 1995; Sommer & Horwitz, 2001). Where reinundation following drought triggers the emergence of macroinvertebrates from resting stages and the emerged animals are faced with inhospitable water quality, there is the danger of 'seed bank' depletion (Arnott & Yan, 2001). This reduces the number of potential colonists available to repopulate the lake when environmental conditions improve. As well as the direct toxic effects of acidity, the absence of vulnerable invertebrate species has also been attributed to metal toxicity (Gerhardt, 1994; Taylor, Rees, & Pascoe, 1994; Wren & Stephenson, 1991) and/or calcium limitation (Omerod & Rundle, 1998).

Human health may also be affected where plumes of acidity and metals (including arsenic) are exported to groundwater that is publicly used (Appleyard et al., 2004; Hinwood, Horwitz, Appleyard, Barton, & Wajrak, 2006).

Some of the changes in aquatic ecosystems that have been attributed to lake acidification may in fact have involved increased exposure to ultra-violet light (due to decreases in DOC concentration, as discussed in Section 2.4.2; Schindler & Curtis, 1997). Although increased light penetration may favour increased algal growth, Schindler et al. (1996) have shown that elevated UV-B radiation negatively influences an enzyme (alkaline phosphatase) that cleaves inorganic P from dissolved organic matter. They concluded that decreases in this enzyme in the presence of ultra-violet radiation could increase P-stress in low nutrient aquatic environments. Bothwell et al. (1994) further found that solar UV-B radiation can reduce the photosynthesis and growth of benthic diatom communities in shallow freshwater, while paradoxically the growth of other algae is increased. They also found that increased UV-B radiation inhibits algal consumers (especially Chironomidae) more than the algae they consume, thus contributing to counterintuitive increases in algae in habitats exposed to UV-B. Nevertheless, epilimnetic phytoplankton in the ocean and in lakes can suffer from photo-inhibition down to depths of several meters (Moeller, 1994). Aquatic vertebrates may also be affected by increased solar radiation. In western USA, pathogen outbreaks in amphibian populations have been linked to climate-induced changes in UV-B exposure (Kiesecker, Blaustein, & Belden, 2001). Amphibian populations have globally suffered widespread declines and extinctions in recent decades.

2.6 A conceptual model of what happens when wetland sediments dry and rewet

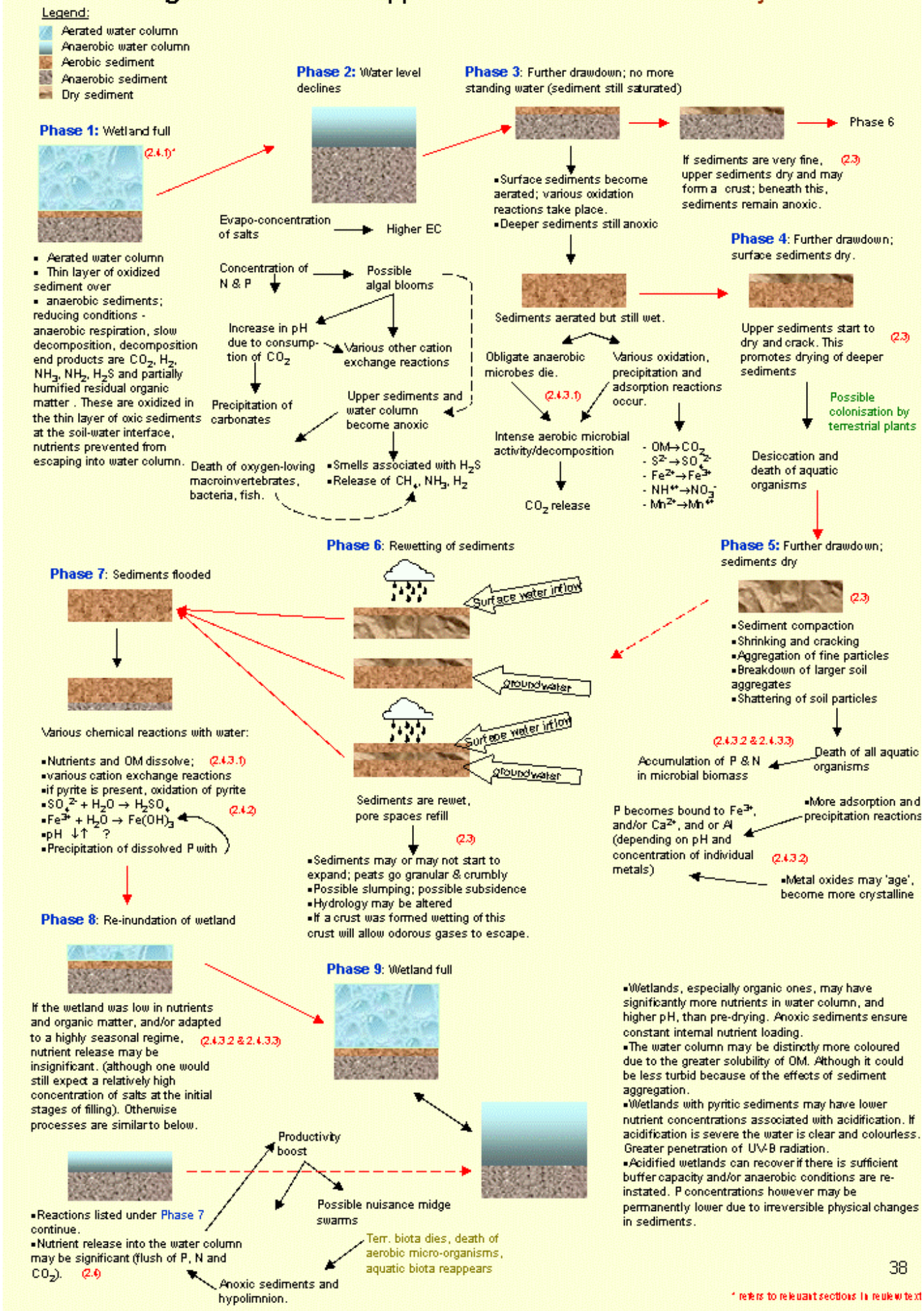
As a partial summary of, and a visual supplement to the literature reviewed, a conceptual model of what happens when wetland sediments dry and rewet is presented in Figure 2.6.1. The model identifies different phases of drying and refilling which should be similar for most drying/wetting events. It is, however, a base model and will need to be adapted to individual wetlands with specific characteristics (such as sediment elemental composition, or the presence of different types of sediments). In addition, the actual processes and effects will depend on a number of factors (see in Section 2.1). Nine phases are identified, ranging from a full wetland through various stages of drawdown and drying, refilling and back to a full wetland. The further along the phases, the less likely under ‘normal’ climatic events/hydrological scenarios, but the more

extreme the consequences will be. Where appropriate, references to relevant sections in this review are made in red brackets.

2.7 Conclusions

This chapter has emphasized that whilst wetlands and their biota are adapted to natural cycles of wetting and drying, extreme or altered wetting-drying regimes have significant impacts on the biogeochemistry of sediments which in turn influences water quality and the ecology of these water bodies. The focus of this review was drought-induced eutrophication and drought-induced acidification, two of the most commonly reported outcomes of drought. Changes to the hydrological regime are most commonly the result of climate change, land management practices (e.g. urbanization, agriculture), rechannelling of surface waters, and over abstraction of groundwater. Because of the natural complexity of wetlands, research from one system, often focussed on specific issues, cannot readily be applied to another system, even if on the surface they might seem similar. Although there are certainly general conventions in response to wetting-drying, this review has pointed out numerous instances of contradictory responses. These differences, more often than not, are primarily the result of differences in sediment characteristics. The conclusion to be drawn then is that before any wetland management decision is made, it is imperative to characterise the sediments. Once such data are available, the literature reviewed becomes much more useful, and wetland managers can invariably move away from the traditional empirical 'black-box' approach taken to wetland management (criticized by Reddy & Patrick, 1993). This is particularly important in a dry continent such as Australia and in view of predicted global climate trends.

Figure 2.6.1: What happens when wetland sediments dry and rewet?



* refers to relevant sections in review text

CHAPTER 3
THE SEDIMENTS OF LAKE GOOLLELAL, SWAN COASTAL PLAIN, WESTERN AUSTRALIA

Abstract

In this chapter physical and bulk sediment characteristics were used to describe the sediments of Lake Goollelal. Two distinct sediments were identified: suspended detrital floc and peat. Both were highly organic, sulfidic and iron-rich. Organic carbon to nitrogen ratios indicate that the peat organic matter (OM) is primarily of vascular plant origin, while the floc is of aquatic (algal) origin. Other sediment proxies appear to support this conclusion. There were higher concentrations of most elements in the floc (exceptions being C_{org}., As, V, and Cr), probably because of more reactive OM and consequently higher iron sulfide concentration which is very efficient at scavenging trace elements from the water column. From the literature, it was deduced that unique microbial ecology and physical structure of the floc must be responsible for the very high N and P concentrations (3.82% and 0.267% respectively), although this certainly needs verification through systematic studies.

The peat has tentatively been classified as an 'aquatic sulfisapric, catotelmic, probably minerogenous, mesotrophic sub-neutral peat', and the floc as a 'limnic sulfidic suspended green detrital floc with *gyttja* characteristics grading into suspended brown detrital floc with *dy* characteristics'. Both sediments became severely water repellent when dried. This study has shown that much can be learned about within-wetland processes by carrying out a few simple sediment analyses and using proxies such as elemental ratios. Because of this, sediment characterisation should be the first step in the development of any wetland management plan.

3.1 Introduction

Lake Goollelal is a small (60.7 ha), permanent (maximum depth at deepest point: ~ 2.1 m to the surface of the consolidated sediment), suburban wetland. It is

the southern-most of a linear wetland series comprising, in a north-south direction, Lake Joondalup, Beenyup Swamp, Walluburnup Swamp and Lake Goollelal (Figure 3.1.1). This chain of wetlands is located within the coastal limestone belt of the Swan Coastal Plain (Allen, 1976), a Quaternary dune system consisting of aeolian sands known as the Spearwood dune system (see Figure 1.1, Chapter 1). Together they comprise the 1400-hectare Yellagonga Regional Park. Lake Goollelal, located ~6.5 km from the coast and ~20 km north of the Perth CBD, lies in a steep-sided interdunal depression and is the highest of the linear series. The lakebed lies at 25.1 m AHD (approx. 10 m higher than that of Lake Joondalup to the north). Although the Yellagonga wetlands are essentially groundwater flow-through systems (Davidson, 1995), the differences in topography have resulted in considerable surface water flow during the winter months from Lake Goollelal towards the lower-lying wetlands to the north (via culverts under roads). In addition there are a number of stormwater drains that feed into the wetlands (Ove Arup & Partners, 1994).

Lake Goollelal is a surface expression of the water table of the superficial aquifer known as the Gnangara mound. A combination of over-abstraction of groundwater, climate change and unfavourable land use practices has resulted in a decline of the regional groundwater table (reported to be as much as 6 metres in some areas of the Gnangara mound, Government of Western Australia, 2003). This has resulted in many of the groundwater dependent seasonal wetlands on the mound experiencing prolonged and more severe summer drying. Hydrographs from the Western Australian Water Corporation show that Lake Goollelal has not dried since at least the early 1950's when measurements began, and in spite of reduced rainfall and increased abstraction, there has been a general rising trend in lake water levels (see Appendix 3.1). This may be related to its distinct hydrological features and possibly also to major roads blocking surface flow to the north (see Figure 3.1.1). There is some suggestion that the overflow capacity (through culverts and drains) is not as great as inflow to the lake (Ecologia Environmental Consultants, 1998). To-date there has been no detailed study into the hydrology of Lake Goollelal, nor its sediments. As with the majority of flow-through wetlands on the Swan Coastal Plain (Townley et al., 1993) the lake captures groundwater on its up-gradient side (i.e. the east/north-east), and must discharge it on the lower, down-gradient side. It has been suggested that the lake may be perched, the water being held there by the peaty

sediments (Brittain, 1990). This is a common feature of deep peats, where hydraulic conductivity is significantly reduced due to the build up of gases (mainly methane). It has been suggested that methane becomes trapped within the peat matrix and that this prevents its saturation (Reynolds, Brown, Mathur, & Overend, 1992).

V & C Semeniuk Research Group (1997) found that 'green clay' of Pleistocene age (i.e. between ~2 million and 10,000 years old) underlies Walluburnup Swamp immediately to the north of Lake Goollelal (see Figure 3.1.1). They contend that most of the wetlands in the Yanchep Suite (of which the Yellagonga wetlands are the southern-most part) are of Holocene age (i.e. ~10,000 years ago to present). At Walluburnup Swamp this 'green clay' affects the flow and discharge of water into and out of the wetland, complicating the hydrology of the wetland. Considering not only the proximity of the two water bodies (they may even have been connected at some stage in the past), and the extent of peat in both, it is not unreasonable to speculate that such 'green clay' (carbonate mud) might also underlay Lake Goollelal and affect its hydrology.

The vegetation of Lake Goollelal falls within the 'Karrakatta Complex, Central and South Complex' and contains vegetation from the 'Herdsman Complex' within the wetland (Heddle, Havel, & Loneragan, 1980). The eastern fringes of the lake consist of sedge communities dominated by *Baumea articulata* or mixtures of *B. articulata* and *Typha orientalis*, with large areas of parkland and other disturbed areas; the western fringes consist mainly of paperbark woodland (*Melaleuca rhaphiophylla*) with some adjoining Jarrah/Marri/Banksia open woodland in the southwest. There are also relatively large disturbed areas on the western fringes of the lake. In addition, there is a chain of islands in the centre of the lake and these are vegetated with *B. articulata*, but also with some isolated, small *M. rhaphiophylla*. Numerous submerged stumps of dead *M. rhaphiophylla* in the southern end of the lake are testimony to previously lower water levels. Aquatic macroinvertebrate richness is low compared to other SCP wetlands, this being dominated by Chironomidae larvae (non-biting midges) and palaemonid shrimps.

The sediments of the lake periphery (the areas that dry annually) are sandy/organic sandy. The lakebed has extensive mucky-peaty sediments overlying quartz sands which in turn overlay calcareous sands. Suspended over the mucky-peaty sediments is a layer of organic detrital floc. The depth of the peat has not been

determined, however, from personal observations during sampling, it is at least 2 metres deep (as far as our corer would go), but is probably substantially deeper. V & C Semeniuk Research Group(1997) measured peat depths of up to 10 m in Walluburnup Swamp. The base of the peat was dated to ~10,000 B.P., making this the oldest known Holocene wetland on the Swan Coastal Plain (V & C Semeniuk Research Group, 1997). It is quite possible that Lake Goollelal sediments are of a similar age.

Since European settlement some 200 years ago, landuse surrounding Lake Goollelal has included market gardens, viticulture, horse agistment, poultry farming, a piggery and other commercial activities (Anon., 2000). Gradually these activities have been replaced by urban development (including stormwater drainage, with occasional accidental spills of raw sewage into the lake), and today there is just one commercial nursery remaining at the south-eastern end of the lake. Despite the organic nature of the sediments, the water column is uncoloured. Over nine years of monitoring (Clark and Horwitz, 2005, see Appendix 3.7), the surface water of the lake has had a pH ranging from ~ 7.2 - 9.7, and an electrical conductivity of between 649 and 1,535 μS cm^{-1}. In terms of phosphorus and nitrogen the lake can be described as oligo- to mesotrophic (mean winter phosphate concentration ~5 μg L^{-1}; mean summer phosphate concentration ~13 μg L^{-1}). However, the sediments have one of the highest total phosphorus and nitrogen concentrations of all of the wetlands on the Swan Coastal Plain (up to 0.2% P and 2.11% TKN; Davis et al., 1993, and this study). Past landuses have also contributed to a build-up of organo-chlorine pesticides in the sediments (chlordane, heptachlor and chloropyrifos; Davis et al., 1993).

This study was carried out as part of a larger study that investigated the effects of drying and rewetting on aquatic organic sediments. As mentioned in Chapter 2, differences in sediment properties are usually responsible for different responses to drying and rewetting. It was therefore deemed imperative to characterise the sediments of the study site. However an examination of the geochemical properties of the sediments of this particular lake is long overdue and justified in its own right. A number of permanent or semi-permanent wetlands with organic-rich sediments exist on the Swan Coastal Plain (and indeed elsewhere in Western Australia), and yet have seldom been described and are thus poorly understood. One

of the objectives of this chapter was to demonstrate how a knowledge of the geochemical properties of aquatic sediments can be used to infer wetland function, and can thus serve as a most valuable aid in making informed management decisions. In addition, since aquatic organic matter is a remnant of the biota that lived within and around the lake during millennia of sediment accumulation, this preliminary description of the geochemical sediment properties may incite future paleolimnological studies designed to reconstruct Holocene environmental conditions on the Swan Coastal Plain.

3.2 Methods

3.2.1 Sample collection and preparation

In order to have site characteristics representative of the whole lake, the lake was divided into two longitudinal and into three horizontal sections, giving six sections. One site was randomly selected within each section, giving six sites (Figure 3.1.1). Sampling was carried out on 24th July 2003 from an aluminium dinghy. Geographical bearings were taken at each site using a Global Positioning System (*Garmin 45*). In-situ water column physico-chemistry (top and bottom) was measured with portable WTW (*Wissenschaftliche Technische Werkstaetten*) multi-meters. Three replicate sediment cores were taken by inserting a 2 m by 0.045 m diameter clear plexitube into the lake sediment to a depth of >0.20 m of consolidated sediment. Lake water was carefully decanted out of the tube. All of the unconsolidated sediment (this will be referred to as 'floc' henceforth) was then carefully decanted into a labelled snap-lock plastic bag which was immediately sealed, squeezing out as much air as possible. The consolidated sediment was emptied into another snap-lock plastic bag, also squeezing out as much air as possible. All three replicate bags from one site were placed into a 20-litre plastic bucket. The bucket was then filled up with floc, and sealed with a tightly fitting lid. The oxygen demand of this 'sacrificial' sediment would be very high, ensuring that the samples remained anoxic (Baldwin, 1996a). Anaerobic samples were required for the experiments and procedures described in Chapters 4, 5 and 6. The buckets were kept in a dark cool-room at between 2-4°C until processing.

In an anaerobic glove-box (*Extech Pty Ltd*) purged with ultra high purity N_2 gas, the three replicate samples of peat and floc from each site were composited,

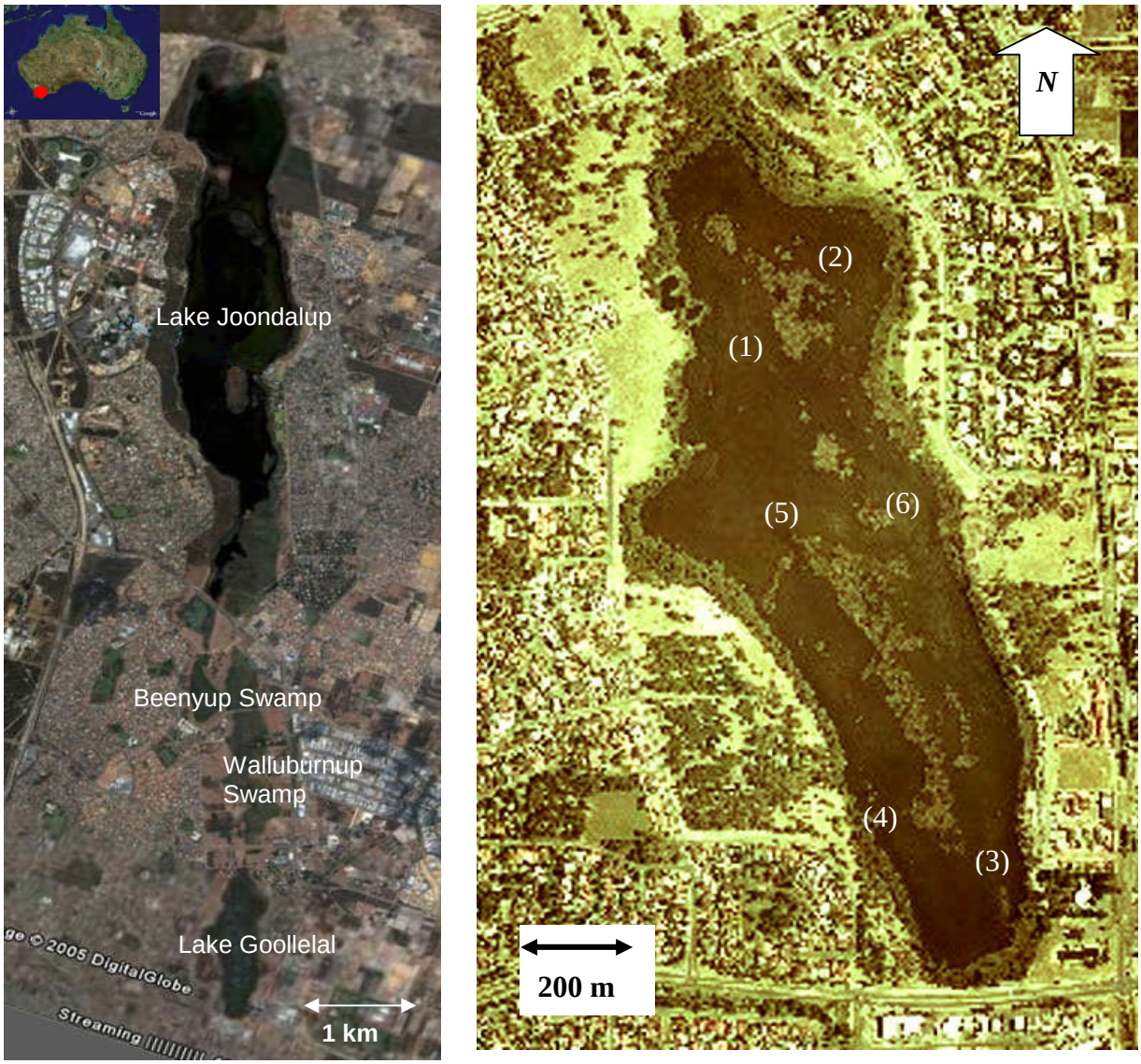


Figure 3.1.1: Aerial view of Yellagonga Regional Park (left), and Lake Goollelal (right) showing the location of study sites. Scales are approximate only. (Satellite imagery courtesy of Google Earth).

thoroughly homogenised, and then sieved (2 mm pore size). Sieved floc 'porewater' was set aside for elemental analysis. Sediment sub-samples were analysed for electrical conductivity and pH (directly [where possible] by inserting probes into wet sediment, and by adding enough double de-ionised water [Milli-Q] to wet sediment to make up a 1:50 sediment:water ratio), water content (determined by weight lost upon air drying in an oven at 35°C and oven drying at 105°C), and Loss on Ignition (LOI) as a surrogate for organic matter content. Further subsamples of each sediment type from each site were dried in an oven at 35°C until a stable weight was attained (this took 12 days to achieve). LOI was determined by first oven-drying (105ºC) ~35

g of air-dried sediment until a stable weight was obtained, and then ashing at 500°C for 16 hours. %LOI was calculated as follows:

$$\%LOI_{500} = ((DW_{105} - DW_{500})/DW_{105}) * 100$$

Carbonates appear not to be driven off by temperatures of ≤500°C (Schulte & Hopkins, 1996). Organic carbon ($C_{org.}$) in the sediment samples was estimated by multiplying %LOI by 0.58. This is a rough estimation based on the assumption that organic matter contains ~58% organic carbon (Nelson & Sommers, 1996).

3.2.2 Elemental analyses by X-ray fluorescence (XRF) spectrometry

The main reasons why XRF spectrometry was chosen for the elemental analysis of these sediments was that it is generally more accurate and quicker than conventional chemical analysis techniques (Karathanasis & Hajek, 1996). The analyses were carried out at the University of Western Australia on a *Philips PW1404* (a sequential wavelength dispersive spectrometer with a 12-place sample changer) using the fused beads method (Karathanasis & Hajek, 1996). Fused beads were prepared as follows. Air-dried sediment samples were ground to a fine powder with mortar and pestle prior to fusion. 7.000 g of Norrish flux 12:22 (mixture of lithium metaborate/tetraborate for XRF) and 0.7000g of sample (resulting in a 10x dilution) were weighed into a 70 ml plastic vial, shaken to homogenize, and then carefully transferred to a platinum crucible. Platinum-tipped tongs were used to place crucibles into a muffle furnace at 1050ºC. After 20 minutes each crucible was gently and carefully swirled to facilitate mixing. The samples were allowed to fuse for a further 20 minutes.

After fusion, moulds were placed on a heatproof tile at the front of the furnace for 2-3 minutes to preheat. Just prior to pouring, a few crystals of ammonium iodide were added to the molten samples in order to increase surface tension of the melt and significantly reduce the amount of residue left in the crucible. Each crucible in turn was picked up with Pt-tipped tongs, swirled gently and poured into the moulds. After cooling, the beads were removed from the moulds and appropriately labelled.

A concurrent loss on ignition (LOI) was determined for each sample fused (at 1050ºC for 40 minutes) as a quality control check. When added to the total of all

other major components the sum should equal ~100%. Existing reference fused beads were used as standards against which oxides and elements were measured.

3.2.3 Other analytical procedures

Total nitrogen was analysed on a *Leco FP428* Nitrogen Analyser by CSBP, Bibra Lake, and total sulfur on a *LabFit CS* Sulphur Determinator by Amdel, Wangara. Because of a strong suspicion of the presence of pyrite in the sediments (see Chapter 6), air-dried samples from two sites (Site 3 and 6) were analysed for chromium-reducible sulfur according to the methods described in Ahern, McElnea, & Sullivan (2004) by the Chemistry Centre (WA), East Perth.

Filtered (0.45 μm cellulose acetate) floc 'porewater' water elemental composition was analysed by ICP-AES (Inductively Coupled Plasma – Atomic Emission Spectrometry) by the Marine and Freshwater Laboratories (MAFRL) at Murdoch University. In addition, as a quality control check, air-dried sediment samples from all sites were digested with *aqua regia* according to the methods described in Chen & Ma (2001), and the digests were also analysed by ICP-AES for total elements by MAFRL. These results were compared to the XRF results.

After an incubation experiment (Chapter 4), and elemental fractionation (Chapters 5 and 6), there was strong indication that the sediment particles may become coated by humic matter upon drying. Therefore, in retrospect, a standard soil water repellence test (molarity of ethanol droplet, MED, - King, 1981) was carried out on finely ground air-dried sediment samples. The MED test measures the molarity of drops of ethanol solutions that infiltrate within 10 s. The more water repellent the soil, the higher the molarity of ethanol needed to penetrate the soil.

3.2.4 Statistical analyses

Tests of normality (Kolmogorov-Smirnov and Shapiro-Wilks in SPSS vs. 11.0 for Windows) were carried out in order to determine whether the distributions of sediment characteristics within sites were normal (i.e. no significant differences between sites). T-tests (also in SPSS) were carried out in order to determine if there were significant differences in any of the sediment characteristics between peat and floc. Simple linear correlations (Pearson's r) were carried out in order to assess relationships between variables. In addition, correlation-based principal component analyses (PCA, using Primer Package for Windows v. 5.2.1) were used to summarise

patterns of (normalised) elemental distribution in sites and sediment types (i.e. peat and floc).

3.3 Results

3.3.1 Water column and sediment description

Table 3.3.1 shows the geographical coordinates and the physico-chemical attributes of the water column of the six Lake Goollelal sites. Water column depth, measured to the top of the floc layer, ranged from 0.88 m (Site 6) to 1.20 m (Site 5). The cool water temperatures (top 12.6 to 14.1°C, bottom 13.0 to 13.9°C) are a reflection of the time of year that sampling took place (winter). Both top and bottom of the water column were well oxygenated (top 10.02 to 10.61 mg L^{-1}, bottom 9.98 to 10.47 mg L^{-1}), although redox potentials were comparatively low (top 59 to 162 mV, bottom –197 to –285 mV). The very reducing potentials measured at the bottom of the water column may have occurred due to overlap with the floc/water interface. pH was well above 7 at all sites (top 7.65 to 8.18, bottom 7.53 to 8.40). EC ranged from 839 to 853 μS cm^{-1} at the top, and from 847 to 1141 μS cm^{-1} at the bottom of the water column.

Table 3.3.1:

Water column physico-chemistry of the six Lake Goollelal sites (sampling date 24/07/2003; mean (standard error))

		Site 1	Site 2	Site 3	Site 4	Site 5	Site 6	Mean
Position (GDA94)		S 31°48.526' E115°48.669	S 31°48.504' E115°48.765'	S 31°49.891' E115°48.958'	S 31°49.130' E115°48.897'	S 31°48.826' E115°48.694'	S 31°48.803' E115°48.867'	
Depth m		1.10	1.00	0.95	0.95	1.20	0.88	1.01(0.05)
Temperature °C	(top)	13.2	14.1	12.6	13	13.5	13.9	13.38 (0.23)
	(bottom)	13.5	13.5	13.5	13	13.9	13.9	13.55 (0.14)
O_2 %	(top)	94.7	99.5	95.3	93.5	101.2	99.9	97.35 (1.32)
	(bottom)	100.4	99.9	94.8	93.2	98.5	95.6	97.07 (1.20)
O_2 mg L^{-1}	(top)	10.2	10.47	10.18	10.02	10.61	10.35	10.31 (0.09)
	(bottom)	10.5	10.4	9.98	9.9	10.22	10.09	10.18 (0.09)
pH	(top)	7.65	8.02	7.97	8.11	8.18	7.87	7.97 (0.08)
	(bottom)	7.67	8.06	7.53	8.15	7.61	8.4	7.90 (0.14)
conductivity μS cm^{-1}	(top)	847	839	841	848	848	853	846 (2.1)
	(bottom)	850	847	1141	849	988	853	921 (49.4)
ORP mV	(top)	117	86	65	59	162	64	92 (16.5)
	(bottom)	-197	-197	-263	-248	-285	-257	-241 (14.8)

Table 3.3.2 gives the descriptions of the different strata identified in the 6 cores taken. All cores had three distinct layers of varying depths: (1) a dark green flocculated suspension that ranged in depth from 0.14 to 0.44 m; (2) a layer

becoming denser with depth, but still suspended, where green grades into brown ranging from 0 to 0.33 m in depth; and (3) a dark brown consolidated mucky peat layer of >0.20 m depth. The peat was predominantly sapric, very fine and structureless (i.e. original plant matter unrecognizable), however, sometimes small pieces of *Melaleuca* bark were evident. The peat also tended to become more consolidated, and distinctly less saturated with depth. Figure 3.3.1 shows an example of a core profile (this one taken from Site 2).

Table 3.3.2:

Description of core strata from six Lake Goollelal sites (boundaries determined visually while still in perspex corer to the nearest cm)

Core strata (m)	**Site 1**	**Site 2**	**Site 3**	**Site 4**	**Site 5**	**Site 6**
Dark green floc	0.14	0.27	0.19	0.175	0.44	0.225
Green floc grading into brown	0.33	0.31	0.30	0.16	0	0.225
Peat (dark brown to black with reddish tinge, sapric with some recognizable *Melaleuca* bark)	>0.20	>0.20	>0.20	>0.20	>0.20	>0.20

Table 3.3.3 shows the physico-chemical characteristics of the six cores. The mean pH of the peat was 6.5, and of the floc 6.8. On average pH of the peat sediment was 1.4, and the floc 1.1 pH units lower than the bottom of the water column. Although the mean pH of the floc was 0.3 units higher than the mean pH of the peat, at Site 4 (south-west corner of lake) the floc pH was slightly lower than that of the peat, while at Site 2 (north-east) the floc pH was 1 pH unit higher than the peat. The 1:50 dilution (please note this means *made up* to 1:50 since samples already contained water) resulted in a mean increase in pH of the peat sediment of 0.33, and of the floc 0.15 units. However the pH of both the peat and floc sediments of Site 6 remained more or less unchanged upon dilution. The mean EC of the peat (359 μS cm^{-1}) was roughly half that of the mean EC of the floc (665 μS cm^{-1}) in the 1:50 dilution. It was difficult to obtain a reading in the undiluted samples due to lack of

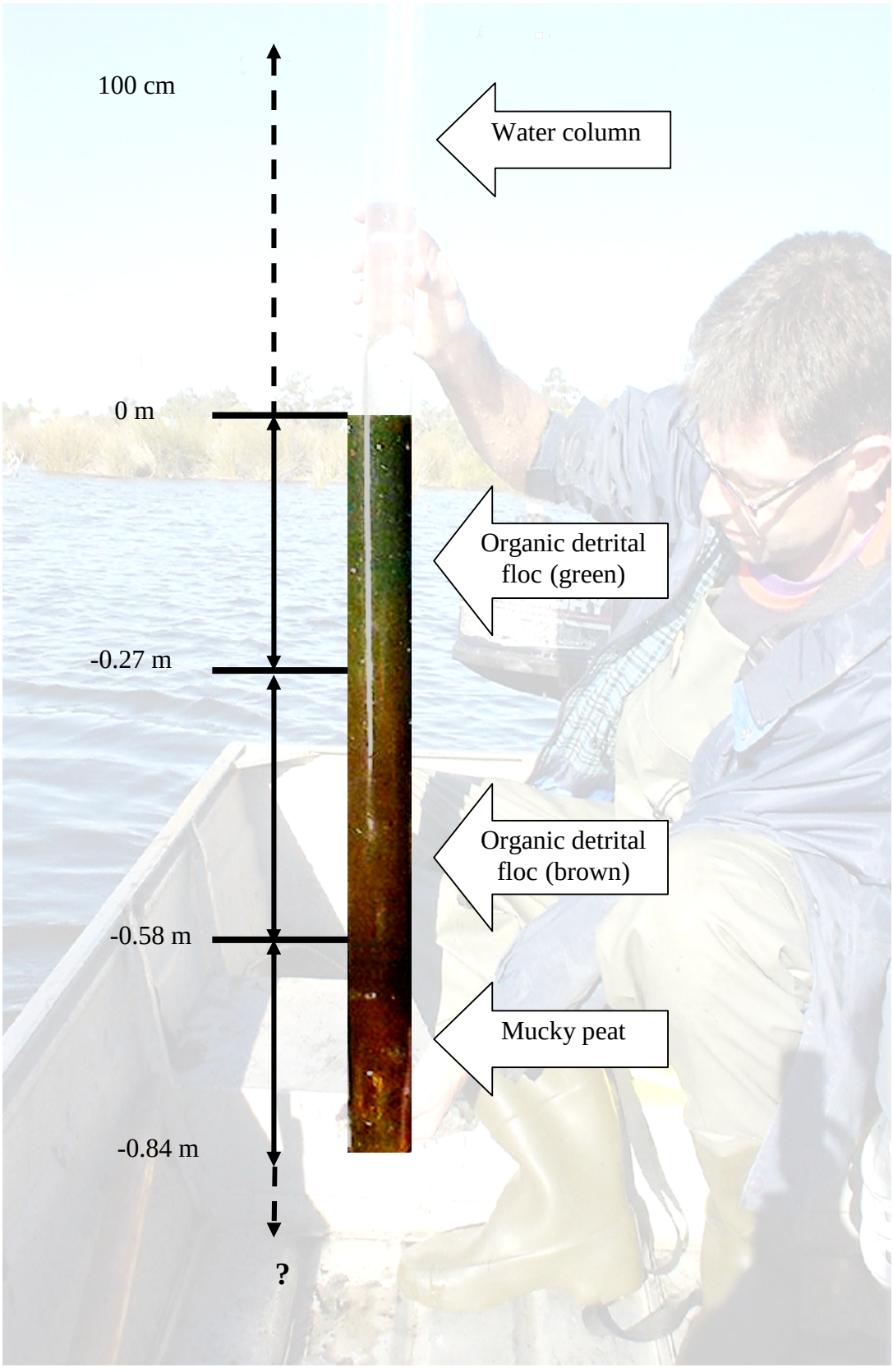


Figure 3.3.1 Example of a sediment core from Lake Goollelal showing the different sediment strata. The brightness of the core in the photograph has been increased in order to highlight colour differences. This core was taken from Site 2.

Table 3.3.3:

Physico-chemical characteristics of the six Lake Goollelal sediment cores

Site	pH straight	pH 1:50 dilution	EC straight	EC 1:50 dilution	%-moisture lost when air dried	%-moisture lost when air-dry sediment was oven died	%-LOI
1 Peat	6.51	6.94	577	405	92.7	4.7	76.9
1 Floc	6.89	7.06	1518	776	95.5	3.3	70.8
2 Peat	5.84	6.30	946	256	88.1	5.6	66.6
2 Floc	6.83	6.84	(no reading)	709	95.2	3.8	72.0
3 Peat	6.85	7.05	(no reading)	468	93.7	4.2	78.6
3 Floc	6.85	6.99	1339	677	95.7	3.4	73.1
4 Peat	7.00	7.18	(no reading)	418	93.0	4.0	82.4
4 Floc	6.86	7.08	1400	737	95.8	3.6	78.5
5 Peat	6.68	7.08	(no reading)	310	91.2	4.5	78.7
5 Floc	6.94	7.18	1518	715	95.3	3.5	68.4
6 Peat	6.24	6.20	710	297	94.7	3.7	78.1
6 Floc	6.49	6.43	756	374	95.8	3.5	70.1
Mean Peat	**6.5** (+/- 0.17 SE)	6.8 (+/- 0.17 SE)		**359** (+/- 34 SE)	**92.2** (+/- 0.96 SE)	**4.5** (+/- 0.26 SE)	**76.9** (+/- 2.19)
Mean Floc	**6.8** (+/- 0.07 SE)	6.9 (+/- 0.11 SE)		**665** (+/- 60 SE)	**95.6** (+/- 0.11 SE)	**3.5** (+/-0.07 SE)	**72.1** (+/- 1.43)

water. On average the peat sediments lost 92.2%, and the floc sediment 95.6% water upon air-drying. A further mean of 4.5% and 3.5% moisture was lost from the peat and the floc sediments respectively when the air-dried samples were oven dried. All sediments were rich in organic matter. Loss on ignition of the peat sediments ranged from 66.6% to 82.4% (equivalent to ~38.6% –47.8% organic C), and of the floc from 68.4% to 78.5% (equivalent to ~39.7% - 45.5% organic C).

3.3.2 Elemental composition

A comparison of total elements as analysed by XRF, *aqua regia*/ICP-AES, Total S analyser, and elemental sequential extraction schemes (Chapters 5 and 6) is given in Appendix 3.4. Tables 3.3.4 and 3.3.5 show sediment elemental composition as percentages and in μmol g^{-1} respectively. Both units are shown to enable comparisons with the literature to be made which are commonly reported in either of these two units. Correlations between individual elements are given in Appendix 3.6. Tables 3.3.4 and 3.3.5 show that the floc contained higher concentrations of the majority of elements. Exceptions were V and Cr, which were significantly higher in the peat than in the floc ($p<0.01$ and $p<0.05$ respectively). Organic C ($C_{org.}$) concentration was also higher in the peat (mean 44.60%) than in the floc (mean

41.83%), as was As (mean peat 0.005%, mean floc 0.002%), but these were not statistically significant on (see Appendix 3.2). Concentrations of N, Na, Al, P, S, K, Ti, Mn, Cu and Zn were all significantly higher in the floc than in the peat (p all between <0.000 and 0.05; Appendix 3.2). Magnesium, Ca, Si, Fe, Rb, Sr and Pb were also higher in the floc than in the peat, but these were not statistically significant. Notable correlations were between P and Al ($p<0.02$) and P and Si ($p<0.01$) in the peat, but between P and Ca ($p<0.02$) and P and As ($p<0.05$) in the floc (Appendix 3.6). In both sediment types Fe and S were significantly positively correlated (peat r= 0.87, $p<0.025$; floc r= 0.98, $p<0.000$). $C_{org.}$ was significantly inversely correlated with Al (r= -0.89)), Si (p< -0.94), and with Ti (r= -0.85), V (r= -0.81) and As (r= -0.85) in the peat; and in the floc positively with N (r= 0.87) and inversely with Si (r= -0.92).

Shapiro-Wilks tests revealed normal distribution of the majority of elements across all six sites in both the peat and floc sediments (Appendix 3.3). Exceptions were floc EC (due to the EC of Site 6 being roughly half as high as in the other sites), peat Na, floc S and Fe, and peat Pb. When Site 6 was eliminated floc EC, peat Na, floc S and peat Pb were no longer significant, however floc Fe still was. This was because once Site 6 was removed, the Fe concentration of the other sites were all roughly equal (which does not equate to a normal distribution).

The spatial distribution of Fe within the peat of the wetland showed a distinct east-west gradient (Figure 3.3.2). Peat P concentration showed a roughly similar trend. An east-west gradient in Fe concentration of the floc was less evident, and if Site 6 was not considered, there was no spatial trend in Fe concentration at all. Phosphorus content of the floc, however, was distinctly higher on the eastern side of the lake (correlation with eastings r= 0.95, see Appendix 3.6). For comparison, Appendix 3.5 lists the elemental composition of the water drained from the floc (‘floc porewater’). Of the elements analysed, only Fe was significantly positively correlated with total floc elemental concentration as determined by XRF (r= 0.93).

The differences in bulk sediment characteristics between the peat and the floc are reflected in Figure 3.3.3. The PCA ordination groups all of the floc samples to the right of the PC1 axis (which explains 46.5% of total data variability). This was influenced by the majority of elements (as discussed above), however the largest contributions were from higher concentrations of Mn, Cu, K, N and also higher EC

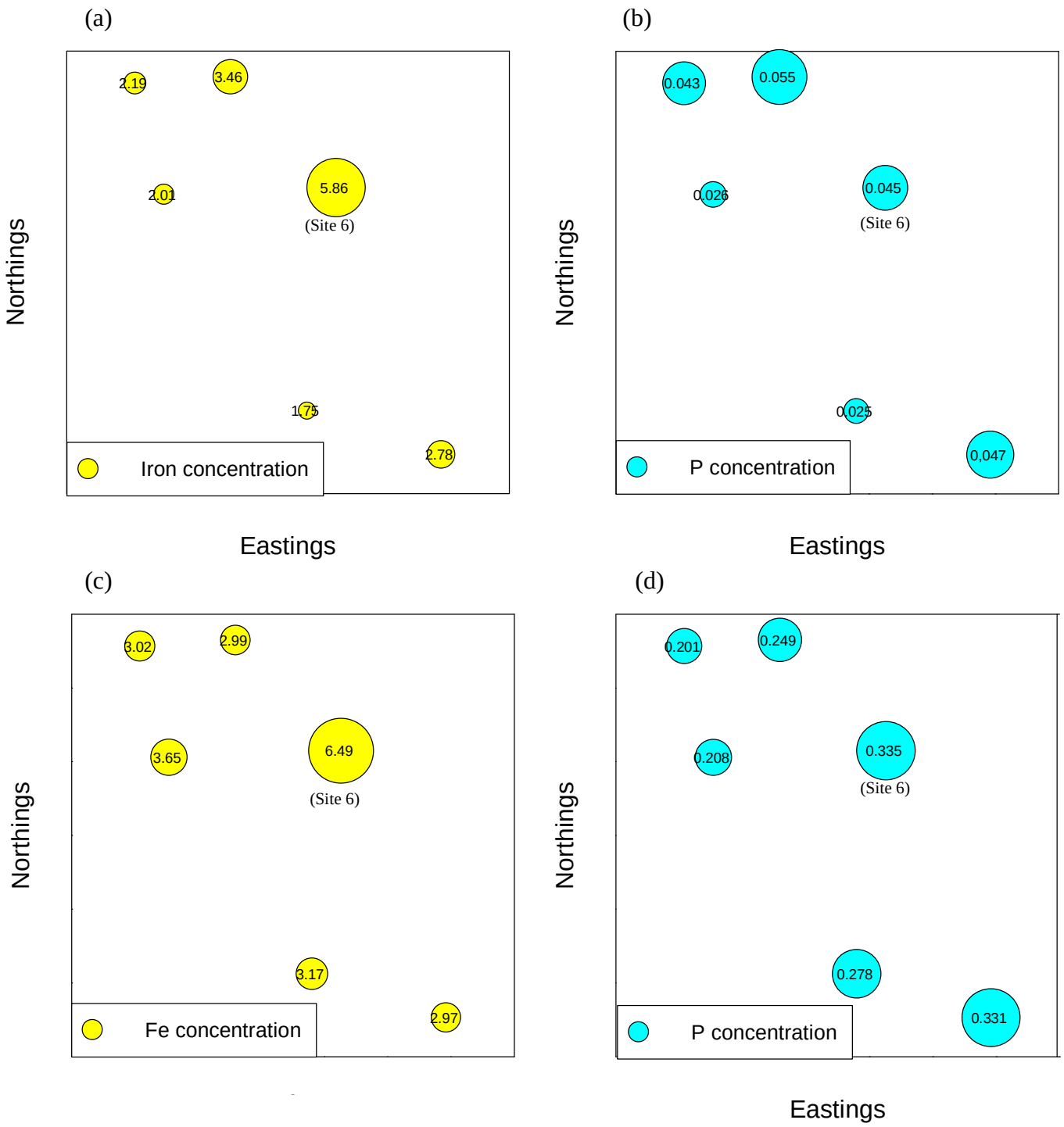


Figure 3.3.2 Comparison of spatial trends in peat iron (a) and phosphorus (b), and floc iron (c) and phosphorus (d) concentration. Figures in bubbles are % weight. Please note difference in magnitude between (b) and (d).

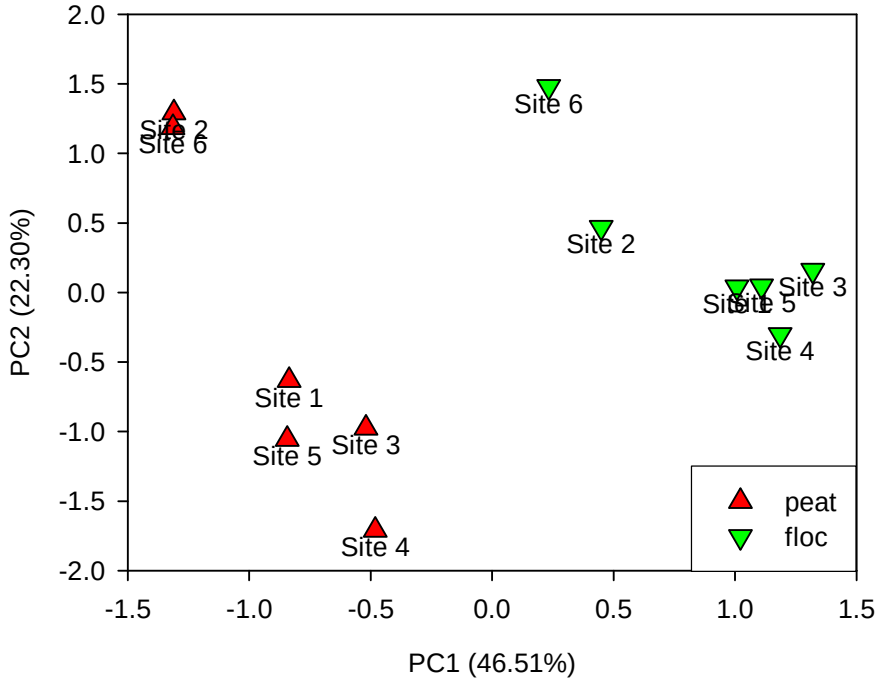


Figure 3.3.3: PCA ordination of sediment bulk characteristics. PC1 and PC2 together explain 68.81% of total data variability**.**

in the floc samples. The PC2 axis (which explains 22.3% of total data variability) groups the sites mainly on the basis of pH and Fe concentrations (pH decreasing, and Fe concentration increasing upwards).

Sediment elemental ratios can provide interesting information regarding the origin of the sediment (e.g. the famous Redfield ratio), nutrient cycling, buffering potentials, and much more. As sediments age and decompose, identifiable molecular fossils become rare in lake sediments, and therefore the characteristics of bulk organic matter are generally more representative of paleoenvironmental conditions (Meyers & Lallier-Vergès, 1999). Ratios of C_{org}.:N, e.g., remain reliable indicators of organic matter sources in spite of the generally low survival rate for most primary organic compounds (Meyers & Lallier-Vergès, 1999). Table 3.3.6 shows some commonly used elemental ratios, and some not so common ones. These are discussed in Section 3.4.2.

Table 3.3.4:

Sediment elemental composition (%oven-dry weight) of six Lake Goollelal sites. (C_{org}= LOI x 0.58; * AR/ICP-AES; # High Temp. Combustion; all others XRF)

		C (org.)	N#	Na	Mg*	Al	Si	P	S#	K	Ca	Ti	V	Cr
Site 1	Peat	44.6	2.04	0.10	0.30	0.43	4.93	0.043	3.86	0.104	1.80	0.013	0.004	0.0085
	Floc	41.1	3.56	0.13	0.35	0.61	6.37	0.201	5.35	0.283	2.71	0.042	0.002	0.0051
Site 2	Peat	38.6	1.91	0.09	0.28	0.56	6.84	0.055	4.12	0.088	1.39	0.020	0.008	0.0142
	Floc	41.7	3.92	0.12	0.34	0.48	7.16	0.249	5.33	0.242	1.74	0.029	0.004	0.006
Site 3	Peat	45.6	2.33	0.09	0.37	0.32	3.90	0.047	5.12	0.078	1.96	0.011	0.005	0.0066
	Floc	42.4	4.09	0.13	0.43	0.59	5.79	0.331	5.26	0.266	1.69	0.032	0.002	0.0047
Site 4	Peat	47.8	2.08	0.15	0.36	0.21	2.71	0.025	4.02	0.078	2.05	0.007	0.004	0.0072
	Floc	45.5	4.19	0.15	0.37	0.55	3.51	0.278	5.68	0.25	1.87	0.033	0.002	0.0061
Site 5	Peat	45.7	2.07	0.08	0.29	0.24	4.49	0.026	3.57	0.104	1.93	0.013	0.003	0.0063
	Floc	39.7	3.45	0.18	0.33	0.51	6.76	0.208	6.10	0.258	3.02	0.034	0.002	0.0066
Site 6	Peat	45.3	2.13	0.08	0.25	0.41	4.90	0.045	6.13	0.06	0.76	0.017	0.006	0.0126
	Floc	40.6	3.73	0.11	0.30	0.46	7.11	0.335	7.57	0.232	1.19	0.022	0.002	0.0071
Mean Peat		**44.60**	**2.09**	**0.10**	**0.31**	**0.36**	**4.63**	**0.040**	**4.47**	**0.09**	**1.65**	**0.014**	**0.005**	**0.009**
S.E.		1.28	0.06	0.01	0.02	0.05	0.56	0.005	0.40	0.01	0.20	0.002	0.001	0.001
Mean Floc		**41.83**	**3.82**	**0.14**	**0.35**	**0.53**	**6.12**	**0.267**	**5.88**	**0.26**	**2.04**	**0.032**	**0.002**	**0.006**
S.E.		0.82	0.12	0.01	0.02	0.02	0.56	0.024	0.36	0.01	0.28	0.003	0.000	0.000

		Mn*	Fe	Cu*	Zn*	As*	Rb	Sr	Ba	Pb*	Cr-S
Site 1	Peat	0.0021	2.19	0.000853	0.0019	0.0044	0.0003	0.0044	0.0147	0.0031	
	Floc	0.0084	3.02	0.005221	0.0049	0.0028	0.0009	0.0051	0.0162	0.0071	
Site 2	Peat	0.0023	3.46	0.000806	0.0023	0.0102	0.0019	0.0038	0.0033	0.0015	
	Floc	0.0069	2.99	0.00243	0.0042	0.0022	0.0021	0.0041	0.0061	0.005	
Site 3	Peat	0.0033	2.78	0.001501	0.0042	0.0025	0.0013	0.0044	0.0165	0.0023	1.46
	Floc	0.0089	2.97	0.007878	0.0087	0.0022	0.0024	0.0061	0.0093	0.0087	1.55
Site 4	Peat	0.0034	1.75	0.001348	0.0022	0.0026	0.0022	0.0069	0.0106	0.0069	
	Floc	0.0095	3.17	0.006179	0.0086	0.002	0.0012	0.008	0.0091	0.0085	
Site 5	Peat	0.003	2.01	0.000535	0.0014	0.0025	0.0014	0.005	0.0081	0.0018	
	Floc	0.0084	3.65	0.006265	0.0058	0.0031	0.0017	0.0067	0.0122	0.0057	
Site 6	Peat	0.0021	5.86	0.000761	0.0032	0.0074	0.0005	0.0027	0.0095	0.0127	1.45
	Floc	0.005	6.49	0.003833	0.0057	0.002	0.0016	0.0033	0.0085	0.0043	4.04
Mean Peat		0.003	3.01	0.001	0.003	0.005	0.001	0.005	0.010	0.005	1.46
S.E.		0.000	0.62	0.000	0.000	0.001	0.000	0.001	0.002	0.002	0.004
Mean Floc		0.008	3.72	0.005	0.006	0.002	0.002	0.006	0.010	0.007	2.80
S.E.		0.001	0.56	0.001	0.001	0.000	0.000	0.001	0.001	0.001	1.24

Table 3.3.5:

Sediment elemental composition (µmol g^{-1}) of six Lake Goollelal sites. (C_{org}= LOI x 0.58; * AR/ICP-AES; # High Temp. Combustion; all others XRF)

		C (org.)	N#	Na	Mg*	Al	Si	P	S#	K	Ca	Ti	V	Cr
Site 1	Peat	37136	1456	43	123	159	1755	14	1204	27	449	2.72	0.79	1.63
	Floc	34221	2541	57	144	226	2268	65	1669	72	676	8.77	0.39	0.98
Site 2	Peat	32140	1363	39	115	208	2435	18	1285	23	347	4.18	1.57	2.73
	Floc	34721	2798	52	140	178	2549	80	1663	62	434	6.06	0.79	1.15
Site 3	Peat	37968	1663	39	152	119	1388	15	1597	20	489	2.30	0.98	1.27
	Floc	35304	2919	57	177	219	2061	107	1641	68	422	6.68	0.39	0.90
Site 4	Peat	39800	1485	65	148	78	965	8	1254	20	511	1.46	0.79	1.38
	Floc	37885	2991	65	152	204	1250	90	1772	64	467	6.89	0.39	1.17
Site 5	Peat	38052	1478	35	119	89	1598	8	1114	27	482	2.72	0.59	1.21
	Floc	33056	2463	78	136	189	2407	67	1903	66	753	7.10	0.39	1.27
Site 6	Peat	37719	1520	35	103	152	1744	15	1912	15	190	3.55	1.18	2.42
	Floc	33805	2662	48	123	170	2531	108	2361	59	297	4.59	0.39	1.37
Mean Peat		**37136**	**1494**	**43**	**127**	**134**	**1648**	**13**	**1394**	**22**	**411**	**2.82**	**0.98**	**1.78**
S.E.		1063	40	5	8	20	198	2	123	2	50	0.39	0.14	0.26
Mean Floc		**34832**	**2729**	**59**	**145**	**198**	**2178**	**86**	**1835**	**65**	**508**	**6.68**	**0.46**	**1.14**
S.E.		686	86	4	7	9	200	8	113	2	70	0.56	0.07	0.07

		Mn*	Fe	Cu*	Zn*	As*	Rb	Sr	Ba	Pb*	Cr-S
Site 1	Peat	0.38	392	0.13	0.29	0.59	0.04	0.50	1.07	0.15	n.d.
	Floc	1.53	541	0.82	0.75	0.37	0.11	0.58	1.18	0.34	n.d.
Site 2	Peat	0.42	620	0.13	0.35	1.36	0.22	0.43	0.24	0.07	n.d.
	Floc	1.26	535	0.38	0.64	0.29	0.25	0.47	0.44	0.24	n.d.
Site 3	Peat	0.60	498	0.24	0.64	0.33	0.15	0.50	1.20	0.11	455
	Floc	1.62	532	1.24	1.33	0.29	0.28	0.70	0.68	0.42	483
Site 4	Peat	0.62	313	0.21	0.34	0.35	0.26	0.79	0.77	0.33	n.d.
	Floc	1.73	568	0.97	1.32	0.27	0.14	0.91	0.66	0.41	n.d.
Site 5	Peat	0.55	360	0.08	0.21	0.33	0.16	0.57	0.59	0.09	n.d.
	Floc	1.53	654	0.99	0.89	0.41	0.20	0.76	0.89	0.28	n.d.
Site 6	Peat	0.38	1049	0.12	0.49	0.99	0.06	0.31	0.69	0.61	452
	Floc	0.91	1162	0.60	0.87	0.27	0.19	0.38	0.62	0.21	1260
Mean Peat		**0.49**	**539**	**0.15**	**0.39**	**0.66**	**0.15**	**0.52**	**0.76**	**0.23**	
S.E.		0.04	112	0.02	0.06	0.17	0.04	0.07	0.14	0.09	
Mean Floc		**1.43**	**665**	**0.83**	**0.97**	**0.32**	**0.19**	**0.63**	**0.75**	**0.32**	
S.E.		0.12	101	0.12	0.12	0.02	0.03	0.08	0.10	0.04	

Table 3.3.6:

Some sediment elemental ratios (w/w above, and mol g^{-1} below) of the six Lake Goollelal sites. Please note: 'C' is organic carbon estimated as 58% of LOI.

		w/w ratios									
		C/N	**C/P**	**N/P**	**C/N/P**	**S/Ca+Mg**	**S/Fe**	**Fe/P**	**Ca/P**	**C/S**	**S/C**
Site 1	Peat	22	1037	47	1037:47:01	1.84	1.76	51	42	12	0.09
	Floc	12	204	18	204:18:01	1.75	1.77	15	13	8	0.13
Site 2	Peat	20	702	35	702:35:01	2.47	1.19	63	25	9	0.11
	Floc	11	167	16	167:16:01	2.56	1.78	12	7	8	0.13
Site 3	Peat	20	970	50	970:50:01	2.20	1.84	59	42	9	0.11
	Floc	10	128	12	128:12:01	2.48	1.77	9	5	8	0.12
Site 4	Peat	23	1912	83	1912:83:1	1.67	2.30	70	82	12	0.08
	Floc	11	164	15	164:15:01	2.54	1.79	11	7	8	0.12
Site 5	Peat	22	1758	80	1758:80:1	1.61	1.78	77	74	13	0.08
	Floc	12	191	17	191:17:01	1.82	1.67	18	15	7	0.15
Site 6	Peat	21	1007	47	1007:47:01	6.07	1.05	130	17	7	0.14
	Floc	11	121	11	121:11:01	5.08	1.17	19	4	5	0.19
Mean Peat		**21**	**1231**	**57**	**1231:57:01**	**2.64**	**1.65**	**75.09**	**46.99**	**10**	**0.10**
S.E.		1	198	8		0.70	0.08	11.63	10.65	0.85	0.01
Mean Floc		**11**	**163**	**15**	**163:15:01**	**2.70**	**1.66**	**14.05**	**8.40**	**7**	**0.14**
S.E.		0	14	1		0.50	0.05	1.62	1.85	0.44	0.01
		molar ratios									
		C/N	**C/P**	**N/P**	**C/N/P**	**S/Ca+Mg**	**S/Fe**	**Fe/P**	**Ca/P**	**C/S**	**S/C**
Site 1	Peat	26	2675	105	2675:105:1	2.10	3.07	28	32	31	0.03
	Floc	13	527	39	527:39:01	2.03	3.09	8	10	21	0.05
Site 2	Peat	24	1810	77	1810:77:1	2.78	2.07	35	20	25	0.04
	Floc	12	432	35	432:35:01	2.90	3.11	7	5	21	0.05
Site 3	Peat	23	2502	110	2502:110:1	2.49	3.21	33	32	24	0.04
	Floc	12	330	27	330:27:01	2.74	3.09	5	4	22	0.05
Site 4	Peat	27	4930	184	4930:184:1	1.90	4.00	39	63	32	0.03
	Floc	13	422	33	422:33:01	2.86	3.12	6	5	21	0.05
Site 5	Peat	26	4533	176	4533:176:1	1.85	3.09	43	57	34	0.03
	Floc	13	492	37	492:37:01	2.14	2.91	10	11	17	0.06
Site 6	Peat	25	2596	105	2596:105:1	6.54	1.82	72	13	20	0.05
	Floc	13	313	25	313:25:01	5.62	2.03	11	3	14	0.07
Mean Peat		**25**	**3174**	**126**	**3174:126:1**	**2.94**	**2.88**	**41.64**	**36.31**	**28**	**0.04**
S.E.		1	511	18		0.73	0.05	6.45	8.23	2	0.00
Mean Floc		**13**	**419**	**33**	**419:33:01**	**3.05**	**2.89**	**7.79**	**6.49**	**19**	**0.05**
S.E.		0	35	2		0.54	0.03	0.90	1.43	1	0.00

3.3.3 Sediment water repellence

Both sediment types shrunk considerably upon drying with cracks forming along horizontal planes. The dry clods were hard with a conspicuous white precipitate formed at the surface (presumably $CaSO_4$). Table 3.3.7 shows that both the dried peat and floc were very severely water repellent. The peat sediment from Site 6 was the most severely water repellent, with a MED of 5.

Table 3.3.7:

M.E.D. (Molarity of Ethanol Droplet) water repellence tests for air-dried Lake Goollelal peat and suspended floc sediment. Water repellence ratings from laboratory tests according to King (1981): <1.0 = low, 1.0-2.0 = moderate, 2.0-3.0 = severe, >3 = very severe.

Peat	MED	Floc	MED
Site 1	4	**Site 1**	3
Site 2	3	**Site 2**	3.5
Site 3	4.2	**Site 3**	3.5
Site 4	4		
Site 5	4	**Site 5**	3.5
Site 6	5	**Site 6**	3
Mean	**4.0 (+/- 0.26 SE)**	**Mean**	**3.3 (+/- 0.12 SE)**

3.4 Discussion

3.4.1 Classification of Lake Goollelal sediments

Many wetland classification schemes exist (*cf.* Chapter 2). For example, based on the Semeniuk (1987) wetland classification scheme, Lake Goollelal would be classed as a mesoscale freshwater, elongate lake (i.e. a permanently inundated basin) with a gradiform vegetation pattern (Semeniuk, Semeniuk, Cresswell, & Marchant, 1990). A wetland classification, however, is not the same as a wetland sediment classification, nor does it take into account sediment characteristics. In the context of this study, developing a sediment classification scheme is important because it helps to understand the processes that underlie the biogeochemical evolution of the sediments and the changes that occur when they are subjected to drying and rewetting. Given the important role that sediments play, not only in response to drought and other disturbances, but also to the general ecology of the wetland, a detailed sediment description or classification is as important, if not more important, than a wetland classification in formulating management strategies.

Unfortunately, not much attention has been given to wetland sediment classification, especially when compared to the classification of soils or even marine sediments. This is beginning to be addressed, though (Schnurrenberger, Russell, & Kelts, 2003; Semeniuk & Semeniuk, 2004). Due to the distinct differences between the two sediment components at Lake Goollelal, these will be dealt with separately. Please also note that only the organic strata of the sediments have been considered in these analyses (i.e. the strata shown in Figure 3.3.1, including peat down to 0.20 m).

3.4.1.1 Peat

Based on soil taxonomy, the consolidated organic component of the Lake Goollelal sediments would be broadly classified as a 'histosol' (Soil Survey Staff, 1999), or an 'organosol' (Isbell, 2002), a group of low-density, organic soils that are formed mainly under cool and water-logged conditions. As such this soil type is analogous to 'peat'. Further subdivision or classification of peats is confusing because different classification schemes (and conflicting terminology) have been developed depending on country, scientific discipline and end-use of the peat (e.g. fuel, agriculture, engineering). Furthermore, the peat literature generally does not deal with truly aquatic, i.e. permanently submerged, organic sediments. Nevertheless, an attempt will be made here to classify the Lake Goollelal peat in terms of (1) particle size; (2) amount of organic matter; (3) physical properties; (4) hydrologic function; (5) origin of the water; (6) botanical origin and (7) chemical properties.

(1) Particle size analysis was not specifically conducted because this is very difficult to define and apply to organic sediments, however, the sediment was very fine and clearly classifies as 'organic mud-sized particles <63 μm, and mostly <4 μm in size' (Semeniuk & Semeniuk, 2004; see also under (3)).

(2) In order to qualify as 'peat', a soil or sediment must have a certain minimum amount of organic matter. This range is very wide in the peat literature (between 5% and >65%), however 30% (depending on the amount of the clay mineral fraction) is the value most often encountered in the international literature (Joosten & Clarke, 2002). In this respect, even if the high end of organic matter content were to be applied, the Lake Goollelal sediment qualifies as 'peat'.

(3) One of the more common subdivisions of peat is based on the degree of decomposition of the original plant matter: fibric (>75% fibres by wet volume); hemic (17-75% fibres by wet volume); and sapric (<17% fibres by wet volume). The Lake Goollelal peat was sapric (also referred to as 'muck'; Mitsch & Gosselink, 2000), to the

point where, when squeezed, all the wet peat escaped through the fingers (i.e. a humification classification of H10 on the von Post scale; Andriesse, 1988). Where saprists contain sulfidic organic material (i.e. potential acid sulfate soils), these are classed as 'sulfisaprists' (Soil Survey Staff, 1999). In addition to the three subdivisions based on %fibres, *Soil Taxonomy* (Soil Survey Staff, 1999) further recognises limnic materials. These are materials deposited in water either by precipitation, through the action of aquatic organisms such as algae and diatoms, or derived from submerged and floating aquatic plants. They include coprogenous earth ('sedimentary peat' formed beneath a body of water that contains at least 50% fish and/or macroinvertebrate-derived fecal pellets), diatomaceous earth and marl. In this sense the Lake Goollelal peat can only partially be classed as limnic because its major components were unlikely to have derived from aquatic organisms (see below).

(4) Peats are commonly subdivided into two layers based on their hydrologic function (see e.g. Clymo, Turunen, & Tolonen, 1998). The acrotelm is the surface layer down to the depth to which the watertable sinks in the dry season, and the catotelm is permanently submerged. In this sense, the Lake Goollelal peat *today* consists of catotelm only. The fact that the peat is sapric, however, suggests either exposure to oxygen at some time during the past, or alternatively, the peat has been submerged for so long (perhaps thousands of years) that anaerobic degradation successfully decomposed the materials. The latter is not improbable considering the high iron concentration of the peat. Lovley (1987) has shown that non-recalcitrant organic matter can be completely mineralised by ferric iron reduction.

(5) & (6) Further subdivisions based on the origin of water (ombrogenous or minerogenous, although a myriad of other terminology exists) and botanical origin (e.g. moss, sedge or wood peat) are difficult to make because, although the lake itself is groundwater-fed (i.e. minerogenous), it is not known whether groundwater moves through the peat, nor whether the peat was minerogenous during its formation (which could have been some thousands of years ago). The sapric nature of the peat suggests low porosity and permeability, and consequently low hydraulic conductivity. Botanical origin is likewise difficult to determine due to the lack of recognizable plant remains. Fragments of paperbark found in the peat may have fallen in relatively recently. Based on the vegetation of the lake today, it is possible that the main botanical source would be *Melaleuca* leaves and bark and sedges. The $C_{org.}$/N ratios throw further light as to botanical origin (see below).

(7) Finally, peats are also classified based on chemical properties (or 'ecological mire types'; Succow, 1988). Based on nutrient concentrations, pH and calcium concentration, the Lake Goollelal peat can be classified as 'mesotrophic sub-neutral' (the other categories being oligotrophic acid, mesotrophic acid, mesotrophic calcareous, eutrophic and salt influenced).

In summary, the Lake Goollelal consolidated sediment will be classified as an aquatic sulfisapric, catotelmic, probably minerogenous, mesotrophic sub-neutral peat. I use the word 'aquatic' to indicate that there are certainly some limnic influences (particularly on the surface), however this probably forms only a minor component of the peat. This classification applies for the top 0.20 m, deeper horizons may have different characteristics. This obviously requires further investigation.

3.4.1.2 Suspended detrital floc

It would be inappropriate to use any of the soil classification schemes to classify the suspended component of the Lake Goollelal sediment, except to use the word 'limnic' (Soil Survey Staff, 1999) which it clearly is. In limnology, two Scandinavian words are commonly used to describe the general character of organic sediments: *dy* and *gyttja* (Wetzel, 2001). In Wetzel (2001, p. 632) these two words are described as follows:

"*Gyttja is a coprogenous sediment containing the remains of all particulate organic matter, inorganic precipitations, and minerogenic matter. In a fresh state, gyttja is very soft and hydrous, with a dark greenish-gray to black color; it is never brown. In a dry state, some gyttjas are hard and black, while others are more friable and lighter in color, depending on the main constituent. The organic carbon content of gyttja is <50%. Dy is gyttja mixed with unsaturated humus colloids. Fresh dy is soft, hydrous, and brown in color. In a dry condition, dy is very hard and dark brown. The organic carbon content of dy and peat is >50%."*

Based on the above descriptions, it would appear that at Lake Goollelal there is *gyttja* (the green floc component) varying in depth from 0.14 m to 0.44 m, grading into *dy*, which varies in depth between 0 m and 0.33 m (see Figure 3.3.1 and Table 3.3.2). The dried composite of the two layers had a greenish-grey colour (the underlying peat was dark brown to black). The green suspended sediment, or *gyttja*, left over from the experiments remained green even after having been kept several weeks in the dark. This strongly suggests that the green pigmentation is not from actively photosynthesising phytoplankton. It could quite possibly be from some sort of anaerobic green bacteria,

possibly a green sulfur bacteria, or even a green non-sulfur bacteria (*cf*. Coolen, Cypionka, Sass, Sass, & Overmann, 2002). *Dy* is poorer in nutrients than *gyttja*, and Wetzel (2001) states that if the C:N ratio is <10, the sediment is neutral humus and *gyttja*; if the C:N ratio is >10 the *gyttja* is mixed with acid humus and the sediment is *dy*. The C:N ratio of the floc was just over 10 (11 on a wt% basis, and 13 on a molar basis), probably reflecting the fact that *gyttja* and *dy* were mixed. Had the green and brown components of the suspended sediment not been combined, it may well have been found that the *gyttja* (green) component would have had a higher pH (quite possibly around 7) than the underlying brown *dy*. In terms of C_{org}. content, both the peat and floc had <50% (although on average there was ~3% more C_{org}. in the peat).

Because the Lake Goollelal floc is obviously flocculated and suspended (i.e. not simply 'unconsolidated'), the terms *gyttja* and *dy* do not entirely satisfactorily describe it. The Encyclopaedia Britannica (http://www.britannica.com) introduces another Swedish term: *äfja*. This is apparently '*finely divided organic remains in colloidal suspension*' (which describes the Lake Goollelal sediment rather well) while *gyttja* is described as being 'a deposit formed from *äfja* that has been oxidised'. Unfortunately no further information on the term *äfja* could be found in any of the major (English) limnological textbooks.

In the fields of geology, paleolimnology and marine science the term 'sapropel' is used to describe '*an unconsolidated deposit composed chiefly of the remains of algae, with mineral grains and spores as minor constituents; these remains accumulate and decompose in anaerobic conditions on the shallow bottoms of lakes and seas. It is distinguished from peat by its high content of fatty and waxy substances (due to algal remains) and small amount of cellulose*' (Lapidus, 1990). When consolidated, sapropel becomes oil shale, bituminous shale, or boghead coal. The presence of 'sapropelic' mudstone layers (probably not unlike the 'green clay' found beneath Walluburnup Swamp; V & C Semeniuk Research Group, 1997) under freshwater lakes in the Coorong coastal plain of southeastern Australia have been used to reconstruct Holocene environmental conditions (Mee, McKirdy, Krull, & Williams, 2004). It is not inconceivable that the Lake Goollelal floc is a present-day analogue of the organic oozes that were the precursors of the green clay formation at Walluburnup Swamp.

Similar research has been carried out on Mud Lake, Florida, where it has been found that, coincident to increases in the paleo-water table, there were shifts in the sediment record from terrestrial and aquatic macrophyte sources within the basal peat,

to a cyanobacterial-dominated sapropel at the surface (which still exists today; Filley et al., 2001). Sapropel development requires anaerobic conditions and this is why its occurrence coincides with higher precipitation and associated higher water levels (e.g. Rossignol-Strick, Nesteroff, Olive, & Vergnaud-Grazzini, 1982). At Mud Lake, Florida, the sapropel has been shown to consist primarily of minute fecal pellets produced predominantly by chironomid larvae (Bradley & Beard, 1969). The pellets themselves consist almost wholly of blue-green algae and their partially digested remains (Bradley & Beard, 1969; Iovino & Bradley, 1969). In the Baltics, lacustrine sapropel, due to its high nutrient and organic matter content, is routinely used as agricultural fertilizer (Bakšienė, 2004; On-line: Anon., n.d.). Perhaps to avoid confusing terminology, a sediment from the Everglades, which would otherwise fit the description 'sapropel' (or perhaps *gyttja* or *dy*) has been termed 'suspended flocculent detrital organic matter' (Childers, Ross, & Leonard, 2003; Noe, Scinto, Taylor, Childers, & Jones, 2003). The term 'benthic floc' has also been used (Turner & Newman, 2005). The benefit of these terms is that the words 'suspended' and 'floc' are highlighted which allows one to pull in the relatively large, but recent, body of floc literature.

Suspended flocculated organic matter develops from the exudates or degradation products of phytoplankton, bacteria and aquatic macrophytes via various physical, chemical and biological means (Leppard & Droppo, 2005). It consists of bacteria, viruses and other small organisms, aggregated humic substances, clay minerals, colloidal iron and manganese oxyhydroxides, biogenic silicates, bacterial envelope fragments, algal scales, cell lysis products, and both mineral and organic nanoscale coatings (Leppard and Droppo, 2005). In eastern Mediterranean sapropels, Passier & de Lange (1998) suggested that microbial sulfate reduction takes place during sapropel formation. Flocs are very porous, rigid and highly hydrated (up to 80% water) which forces their density towards the density of water and prevents them from settling (Droppo, 2001). Suspended organic flocs containing humic substances can have remarkable long-term stability with residence times of centuries (Wilkinson & Reinhardt, 2005). Childers et al. (2003) suggest that in the Everglades marsh drawdown is the primary mechanism by which floc becomes part of the consolidated sediment component. Wetzel (2001) states that the amorphous particles of organic flocs contain appreciably less recalcitrant organic matter than do morphologically distinguishable particles that are clearly plant fragments. This colloidal organic matter is susceptible to appreciable bacterial degradation, and is also very digestible, thus potentially supporting

better growth of detritivous animals (although this has not been researched much to date; Wetzel 2001).

In conclusion, the suspended component of the Lake Goollelal sediment will be classified as 'limnic sulfidic suspended green detrital floc with *gyttja* characteristics grading into suspended brown detrital floc with *dy* characteristics'. This is the first time that this sediment type has been characterised for the Swan Coastal Plain, and there is obviously a need for limnologists to agree on a common terminology.

3.4.2 Sediment bulk characterisation

3.4.2.1 Peat

Elemental composition forms the basis for the classification (see above) of the Lake Goollelal peat as a sulfisaprist, or a sulfidic peat. The mean total sulfur (TS) concentration of 4.47% compares with a world average TS content in organic soils of 0.5% in eutrophic peats and 0.1% in oligotrophic peats (the range being 0.004 to 4.0%; Lucas 1982 cited in Andriesse, 1988). However, TS in the Lake Goollelal peat was lower than the mean TS in Dellwig et al.'s (2002) sulfidic coastal peats from northwestern Germany which ranged from 5.8% to 8.4%, and also much lower than that found in the basal peat of a core from Spoonbill Lake, Stirling (8.8%; Appleyard et al., 2004). However, higher strata of Appleyard et al.'s core had very similar TS concentrations (3.8% - 4.6%). The highest TS concentration in *Sphagnum* bog peat from the Australian Alps was 2.575% in the sapric layer (Grover, McKenzie, Baldock, & Papst, 2005). The chromium-reducible S (S_{Cr}) content of 1.46% is an indication of how much inorganic S in the Lake Goollelal peat would potentially oxidise under aerated conditions. This figure is possibly slightly underestimated (Dr. Barry Price, pers. comm.) because the analysis was performed on air-dried sediment (i.e. some of the reduced S would have oxidised upon drying). Nevertheless it exceeds the NSW ASSMAC action guidelines (i.e. there is risk of an acid sulfate soil issue and the need for an acid sulfate soil management plan with development approval; Acid Sulfate Soils Laboratory Methods Guidelines Manual, 1998).

Iron content of the Lake Goollelal peat (mean 3.01%, but locally as high as 5.86%) is similar to those reported in Dellwig et al. (2002; mean 3.1% - 5.4%) but is very high compared to world averages of 0.5% in eutrophic peats and 0.1% in oligotrophic peats (Lucas 1982 sourced in Andriesse, 1988). It is also high by Swan Coastal Plain standards, with only Herdsman Lake (up to 8%) and Lake Monger (up to 32.4%) having higher concentrations (Davis et al., 1993). The spatial trend in sediment

Fe concentration is most likely a reflection of the fact that Fe-rich groundwater enters the lake on the up-gradient, eastern side.

Dellwig et al. (2002) used the correlation between TS and available Fe ($Fe_{avail.}$) to show the proportion of available Fe that has been converted to pyrite (FeS_2). The calculation of $Fe_{avail.}$ (Brumsack, 1988, cited in Dellwig et al., 2002) is based on the assumption that silicate-bound Fe (which is not available in the early stages of pyrite formation) amounts to ~20% of the Al content:

$$Fe_{avail.} = Fe - (0.2 \cdot Al)$$

As most Fe from sheet silicates is characterized by extremely high half-lives towards the reaction with dissolved sulfide, this Fe is not available in the early stages of pyrite formation (Dellwig et al., 2002). Figure 3.4.1 shows the relationship between TS and $Fe_{avail.}$ in the peat and floc sediments. The graph indicates that 76% of $Fe_{avail.}$ in the peat sediments has been converted to pyrite (i.e. FeS_2) or FeS. This is consistent with the fact that 75%/76.7% (mean of Sites 3 and 6 for wet and dried peat respectively) of total Fe was associated with oxidisable sulfides (Chapter 6). Apart from one site (the Site 6 peat, which had by far the highest Fe content), most of the samples in Figure 3.4.1 veer to the left of the theoretical pyrite ratio, indicating

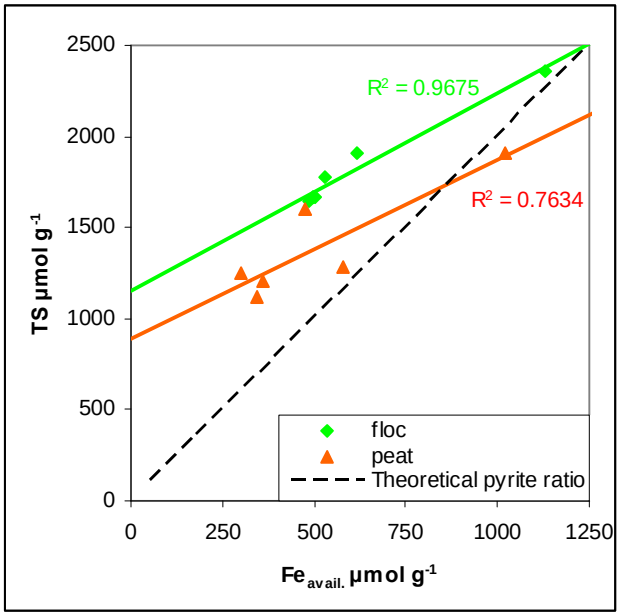


Figure 3.4.1: Scatter plot of total sulfur (TS) versus available iron ($Fe_{avail.}$) of the peat and floc sediments from Lake Goollelal. The dashed line shows the theoretical pyrite ratio**.**

'excess S' (or conversely, Fe limitation with regards to pyrite formation). This 'excess S' could be associated with other metals such as for example Zn (which was also positively, but not significantly, correlated with TS, r=0.79), or, more likely, it is present as reduced organic S compounds. Comparison of $S_{KClO_3}$and S_{Cr} (Chapter 6) suggests that ~⅓ of TS could be organic S. This is low (and consistent with a lack of correlation between S and C_{org}., see Appendix 3.6) considering that organic S is usually the dominant form of S in freshwater wetland sediments (Berner & Raiswell, 1983; Giblin & Wieder, 1992; Luther & Church, 1992), and probably reflects the high Fe concentration of the Lake Goollelal sediments. The formation of organic S compounds competes with Fe sulfide formation, and Fe limitation may be an important factor contributing to organic S enrichment in the humic fraction (Hartgers et al., 1997; Luther & Church, 1992). The S:C_{org}. ratios of the peat (mean 0.10 on a %wt basis) compare to a S:C_{org}. ratio of 0.36 for 'typical' oxygenated marine sediments (Berner & Raiswell, 1984). These reflect the higher sediment organic matter content and lower sulfate concentration in freshwaters compared to sea water.

The C_{org}.:N ratio is used to distinguish between the origin of sedimentary organic matter from aquatic as opposed to land sources. This is based on the characteristic differences in the C_{org}.:N ratios of algae and vascular plants. Typically, organic matter of algal origin will have a molar C_{org}.:N ratio of between 4 and 10, whereas vascular land plants produce organic matter with C_{org}.:N of >20 (Meyers & Lallier-Vergès, 1999). The C_{org}.:N ratios of the Lake Goollelal peat of 25 then suggests that the peat has originated primarily from land-based (possibly including emergent sedges that are not exclusively land-based) vascular plants. Peat N content (mean 2.09%) compares with a reported world average of 2.5% for eutrophic peats and 1.0% for oligotrophic peats (Lucas 1982 sourced in Andriesse, 1988), while P concentrations (mean 0.040%) match the reported world average for oligotrophic peats. The C_{org}.:P ratio (mean 3174 on a molar basis) further supports the suggestion that the Lake Goollelal peat originated from vascular plants, rather than from algae, since this is substantially higher than the typical ratio of 100 for freshwater phytoplankton (Cook & Kelly, 1992), and also substantially higher than the C_{org}.:P ratio of the floc (mean of 419 on a molar basis, see below).

The Fe:P ratio gives an indication of how much Fe is available to bind P and has important consequences for P-release under both anaerobic and aerated conditions (Giordani, Bartoli, Cattadori, & Viaroli, 1996; Jensen, Kristensen, Jeppesen, & Skytthe,

1992). Jensen et al. (1992) found that the increase in total P concentration in Danish lakes from winter to summer was lowest in lakes with high Fe:P ratios. They suggested that provided the Fe:P ratio is >15 (by weight) it may be possible to control internal P-loading by keeping the sediment oxidised. By analogy then, if the ratio is lower than this, there will not be enough Fe to bind the P, and P will be released even under oxic conditions. The Fe:P ratios of the Lake Goollelal peat were very much higher than 15 (*viz*. 79 on a %wt basis), although most of the Fe was present as sulfides rather than (oxy)hydroxides. This could indicate that P release from the Lake Goollelal peat would be limited under most conditions. Giordani et al. (1996) later also found that in spite of strong reducing conditions phosphate (and sulfide) release was weaker in iron-rich sediments. The positive correlation of P with Al ($p<0.02$), and lack thereof with Fe or Ca, suggests that much of the sediment P is associated with Al, or organic Al complexes. This is consistent with findings presented in Chapter 5 where ~50% of total extractable P and ~50% of total extractable Al were in the NaOH (i.e. humic acid) fraction. Aluminium, being redox insensitive, would only release P under alkaline conditions. The Ca:P ratio should give an indication of the sediment's ability to absorb P under high pH values. High pH typically occurs during periods of high productivity, and the co-precipitation of P with $CaCO_3$ can be an effective P buffer if enough Ca is available. Based on the Ca:P ratio, the Lake Goollelal peat then has a ~6 times greater P buffer capacity at high pH (36 on a molar basis) than the floc (6 on a molar basis). This has come about mainly because of the much smaller P content of the peat as compared to the floc, rather than differences in Ca content (see Tables 3.3.4 and 3.3.5).

Calcium content of the Lake Goollelal peat (mean 1.65%) compares with a world average of 2.0% for eutrophic and 0.3% for oligotrophic peats (Lucas 1982 sourced in Andriesse, 1988), placing the Lake Goollelal peat in the mesotrophic range. Calcium content of the Lake Goollelal peat is low compared to that reported by Grover et al. (2005; 3.3% - 8.6% from fibric to sapric) for bog peat in the Australian alps. It is also low considering its geologic setting and may be an indication of a large separation between the underlying limestone lithology and the surface peat layer (i.e. the peat is probably very deep). Lucassen et al. (2002) used the S:(Ca+Mg) ratio to assess the drought-induced acidification potential of mires in the Netherlands. They found that desiccation led to severe acidification when the sediment S:(Ca+Mg) ratio exceeded 2:3 (or conversely 0.67:1). The S:(Ca+Mg) ratio of the Lake Goollelal sediments (mean 2.64 on a %wt basis and 2.94 on a molar basis) was nearly four times higher than this and therefore suggests a significant potential for acidification (see Chapter 4).

Concentration of the other base cations (Mg: 0.24%, K: 0.09%) also fall into mesotrophic range based on world averages, however Na content of the Lake Goollelal peat (0.10%) is higher than that recorded for eutrophic peat (0.05%; Lucas 1982 sourced in Andriesse, 1988). This may be a reflection of the marine influence during peat formation (which was also responsible for high S content). Silicon content of the Lake Goollelal peat (4.63%) compares to a reported world-average of 5.0% for eutrophic peats and 0.5% for oligotrophic peats (Lucas 1982 cited in Andriesse, 1988).

In terms of trace elements, a comparison with other world-wide peats is difficult because of a paucity of information and large variability due to a number of reasons. Peat content of Cu and Pb are very similar to the reported world-averages for eutrophic peats, while Mn and Zn are similar to those reported for oligotrophic peats (i.e. they are on the low side). Cr content (mean 0.0090%) is very high compared to Dellwig et al.'s (2002) coastal peats (0.0012% - 0.0039%); and is also one of the few elements (along with V and As) whose concentration was higher in the peat than in the floc. Not enough information exists to determine whether this relatively high Cr (and V) content is of anthropogenic or natural origin. It may be related to the origin of the peat, or even come from paleo-atmospheric deposition (Krachler, Mohl, Emons, & Shotyk, 2003). Positive correlations of Cr with Al ($p<0.05$) and Si ($p<0.10$) suggests association with aluminosilicates. Another element which was higher in the peat than in the floc was As. Interestingly there was a lack of correlation between As and Fe, and As and S (which would indicate association with iron sulfides), but a very strong positive correlation between As and Cr ($r=0.99$), as well as both of these elements with Al and Si, suggesting association of both As and Cr with aluminosilicates. Arsenic content of the Lake Goollelal peat (0.005%, or 50 mg kg^{-1}) is high compared to Dellwig et al.'s (2002) coastal peats (6 – 16 mg kg^{-1}), and much higher than that reported for Florida histosols (highest concentration: 5.6 mg kg^{-1}; Chen, Ma, & Harris, 2002). Davis et al. (1993) measured up to 225 mg kg^{-1} in Lake Goollelal sediments, and on the Swan Coastal Plain wetlands, only Lake Monger (up to 428 mg kg^{-1}), a polluted lake, had higher sediment As concentrations. By comparison, core samples from Spoonbill Reserve, Stirling (where groundwater acidification is an ongoing problem) contained between 94 and 300 mg kg^{-1}; Appleyard et al., 2004).

3.4.2.2 Suspended detrital floc

Comparison of the floc elemental composition is difficult because there are very few published reports on elemental composition of such sediments (and none in

Australia). The rich floc literature deals primarily with physical characteristics of flocs rather than their chemical composition. There are publications on the chemical properties of marine sapropels (mainly from the eastern Mediterranean), however few of these report on total elemental composition and are probably not suitable as comparisons due to differences between marine and freshwater environments. One of the more obvious differences between the peat and floc sediments was that the concentration of most elements was higher in the floc than in the peat. The main reason for this may be that metal sulfides in the water column very efficiently scavenge trace elements (Passier et al., 1999). The reason for the high P content may be very efficient scavenging by microbes in the floc (Noe et al., 2003). As mentioned previously, these qualities – high nutrient levels and trace elements – make freshwater sapropel an attractive renewable resource for use as agricultural fertilizers in the Baltics. The only (nearly) complete set of data on freshwater 'sapropel' elemental composition was found on the *Saprek* website (http://www.sapropel.lv/), a commercial supplier of sapropel fertilizers. Where appropriate, the Lake Goollelal floc composition will be compared to this.

Sulfur concentration of the Lake Goollelal floc (5.58%, but locally as high as 7.57%) is high by most standards. *Saprek* reported figures of <1% for all of their samples from two Latvian lakes. Bates, Spiker, Hatcher, Stout, & Weintraug (1995) recorded a mean of 3.30% in 1.5 m of sapropel from Mud Lake, Florida. Chromium-reducible sulfur was also high with a mean for Sites 3 and 6 of 2.8% (twice that of the peat). Iron content was likewise high (3.72%) compared to the *Saprek* figure of 0.52% (mean between 3-5 meters), but not much higher than that of the peat (3.01%). Fe concentration in benthic floc from the northern Everglades ranged from 0.14% to 0.76% (Turner & Newman, 2005). The scatter plot in Figure 3.4.1 indicates that ~97% of Fe_{avail}. (as opposed to only ~76% in the peat) has been converted to pyrite, a figure somewhat higher than the 92% (mean of Sites 3 and 6) of Fe associated with oxidisable sulfides (i.e. Fe_{KClO_3}, see Chapter 6). The discrepancy may lie in the fact that only two sites were analysed for Fe_{KClO_3}. The TS:Fe_{avail}. regression line is above the theoretical pyrite line, and also above the peat regression line suggesting that there was slightly more 'excess S' in the floc than in the peat. However, comparison of S_{KClO_3} and S_{Cr} (Chapter 6) also indicates an organic S content of ~1/3 of TS. Again, this may be due to the fact only two sites were analysed for S_{KClO_3} and S_{Cr}., but the presence of mono

sulfides would also create this sort of distortion. It may be beneficial to further investigate these interesting relationships.

The mean S:$C_{org.}$ ratio in the floc (0.14) was also lower than 0.36 (the 'normal' ratio for marine sediments), but higher than that of the peat (0.10). This may be indicative of a higher degree of anaerobia in the floc (since more S relative to $C_{org.}$ is being retained). This is based on the assumption that as SO_4^{2-} is reduced, organic matter is oxidised, and thus lost from the system (Berner & Raiswell, 1983). This then is consistent with the fact that there was more S_{Cr} and S_{KClO_3} (Tables 3.3.4 and 3.3.5) in the floc than in the peat. A higher S: $C_{org.}$ ratio may also be the result of the nature of the organic matter. More reactive or labile organic matter would react more quickly with SO_4^{2-}, and more Fe would be converted to pyrite (see Figure 3.4.1). Having said this, the reactivity of organic matter and anaerobia are certainly interlinked. Thus, (although this is yet to be agreed upon) in addition to being able to distinguish between marine and freshwater sediments (Berner & Raiswell, 1983), the relationship between S and $C_{org.}$ could be used to distinguish between different types of freshwater organic sediments.

The large difference between the $C_{org.}$:N ratios in the peat and the floc, however, is the strongest indicator that the organic matter contained within them have different origins. A $C_{org.}$:N of 13 (on a molar basis) suggests that the organic matter is predominantly of (autochthonous) aquatic origin, probably a mixture of algal and vascular plant contributions (which is expected for most lakes; Meyers & Lallier-Vergès, 1999). $C_{org.}$:N ratios in benthic floc from the northern Everglades were very similar, ranging from 11 to 15 (Turner & Newman, 2005). Interestingly, N concentrations of this benthic floc were also very similar to those in this study (range of 2.51% to 4.58%). With 3.82%, N content was on average 83% higher than that of the peat. This is certainly in part a reflection of the source of the organic matter (terrestrial plants being rather impoverished in terms of both N and P compared to aquatic plants; Ruttenberg & Goñi, 1997). However it has also been suggested that proteinaceous materials may be protected from degradation by incapsulation in sapropelic organic matter (Knicker & Hatcher, 2001). Nitrogen was significantly positively correlated with $C_{org.}$ (r=0.87), which it was not in the peat, suggesting that much of the floc organic matter may be nitrogenous organic matter. Phosphorus content of the floc (mean 0.267%) is extremely high (7 times higher than that of the underlying peat), although one of the two *Saprek* Latvian lakes had a mean of 0.271%, while the other had 0.104%.

Interestingly, P concentration varied considerably with depth of the sapropel in these lakes. In the Everglades, Childers et al. (2003) reported floc P content ranging from 0.04% to 0.08%, while Turner & Newman (2005) reported ranges of between 0.031% to 0.162%. The C_{org}.:P ratio of the Lake Goollelal floc (419 on a molar basis) further supports the view that the Lake Goollelal floc is derived from aquatic rather than terrestrial sources.

Analogous to the huge difference in P content of the two sediment types, there was a difference in the Fe:P ratio of similar magnitude. The mean Fe:P ratio of the floc of 14 (on a molar basis), compared to 75 in the peat, places it below the threshold of 15 proposed by Jensen et al. (1992) where P release can be controlled by keeping sediments oxidised. This suggests that the floc would release P under both anaerobic and oxic conditions.

Calcium content of the floc (mean of 2.04%) compares to a mean of 1.56% and 0.96% for the two *Saprek* Latvian lakes, and a range of 1.11% to 6.24% (although one site had 20.46%) in the Everglades benthic floc (Turner & Newman, 2005). Because of its high P content, the Ca:P ratio in the Lake Goollelal floc is low with 6 (molar basis, or 8.4 on a %wt basis) and indicates poor P buffer capacity at high pH. Ca:P ratios in the Everglades benthic floc were all much higher than this, ranging from 26 to 61 on a %wt basis, with the calcium rich site having a ratio of 660 (Turner & Newman, 2005). Phosphorus was not positively correlated with any other element, making it difficult to deduce its main form. Interestingly, P was negatively correlated to Ca (r= -0.89), meaning that sites with lower Ca concentration had higher P concentration. This may be because there will be less Ca in sites of lower pH, and the sites with lower pH, in turn have more Fe and Al to which P can bind. Sequential extraction (Chapter 5) determined that the main form of P in the wet floc was in the organic fractions (primarily in the un-extractable, residual fraction). The S:(Ca+Mg) ratios did not differ much from those of the peat (mean of 2.94 on a molar basis in the peat, compared to 3.05 in the floc), also implying a significant potential for acidification.

Comparison of all other elements with *Sapreks* website reveals that with the exception of Zn, the Lake Goollelal floc had much higher concentrations of all elements than the two Latvian lakes. The main reason for this is presumably the sulfidic nature of the Lake Goollelal sediments which, as previously mentioned, are efficient scavengers of trace metals. The lack of correlation between Si and Al in the Lake Goollelal floc (contrary to the peat) suggests that Si in the floc may be present as biogenic silicon (e.g.

diatom spicules), rather than as aluminosilicates. The negative relationship between Si and C_{org}. (r= -0.92), then, might be considered puzzling. A plausible explanation for this would be that sites with higher algal (diatoms and the like) input have more reactive C that is quickly mineralized, whereas sites with proportionately less of this (i.e. more input from vascular plants), will have proportionately less diatom residue (i.e. less Si), but more recalcitrant organic matter.

The lack of correlation between the floc bulk composition and that of the floc pore water (Appendix 3.5), apart from that of Fe, suggests a lack of flux between the floc and water column. Exactly why this is requires systematic investigation, however it does explain the striking difference in floc nutrient concentrations and that of the water column (*cf.* Appendix 3.7). The floc appears to be a stable and inert sediment with great scavenging capacity, and thus an impressive sink for nutrients and other elements. It may also act as a physical barrier between the underlying peat and the water column, preventing geochemical exchange between the peat and the water column. This would also be a contributing factor to why the lake is uncoloured, unlike most organic rich wetlands which tend to be stained.

3.4.3 Water repellence

The drying-induced water repellence of the peat and floc should not have come as a surprise considering the organic nature of these sediments. However, water repellence is not something that is usually associated with 'wetland' soils. In fact this is probably the first report of drying-induced water repellence in (permanently inundated) wetland sediments (even though Soil Taxonomy (Soil Survey Staff, 1999, p. 28) lists as one of the characteristics of coprogenous earth (being one of the limnic materials): '*….shrinks upon drying, forming clods that are difficult to rewet….').* There have been a number of reports of soil water repellence induced by humic acids from peats (e.g. Lichner, Babejova, & Dekker, 2002) and of water repellent dry peat soils (e.g. Dekker & Ritsema, 1996; Valat, Jouany, & Riviere, 1991). Water repellence has been typically attributed to the presence of hydrophobic organic substances forming a coating over the surface of soil particles (Ma'shum, Tate, Jones, & Oades, 1988). Some naturally occurring hydrophobic organic substances responsible for water repellence are *n*-alkanes, olefines, terpenoides, monoketones, β-diketones and polyesters of hydroxy-fatty acids (Doerr, Shakesby, & Walsh, 2000). All of these abound in peat (particularly in highly humified peat), and sediments derived from algae, such as the floc, may have a particularly high content of fatty and waxy substances (Lapidus 1990). Not only the

quantity, but also the quality of these substances determines the degree of water repellence (Ellerbrook, Gerke, Bachmann, & Goebel, 2005; Ma'shum et al., 1988). Thus even wetlands with very little organic matter may develop water repellence upon drying.

The effect that drying-induced hydrophobic coatings can have on wetland sediments and water quality after reflooding has not been previously considered. In Chapter 4 some of these effects (particularly in relation to acidification and eutrophication) will be demonstrated and discussed. More research in this regard is required; the studies presented in this thesis are only a beginning.

3.5 Conclusions

The sediments of Lake Goollelal are interesting (to say the least) in terms of potential for paleolimnological reconstruction, as well as in terms of limnological processes. It is fascinating to think that a layer of loose, suspended detritus, barely 50 cm thick, might play such a dominant role in the biogeochemical processes of this water body. The significance of such nanostructures (aquatic flocs being an aggregation of nanostructures), in terms of ecosystem function, and indeed for the sustainability of life itself, has recently been emphasized by Buffle (2006, p.155): '*These basic microstructures are themselves key elements of the whole ecosystem, just as cells and tissues are the key elements of a complete living organism'.* Much is still to be learnt. Lake Goollelal offers opportunities for research in many aspects of limnology, biogeochemistry, the study of organic matter, paleolimnology, and much, much more. As such it is fitting for the lake to be granted top management and conservation status. In terms of management of the Swan Coastal Plain wetlands, and indeed wetlands elsewhere, this study has shown that much can be learned about within-wetland processes by carrying out a few simple sediment analyses. Sediment characterisation (and univariate, bivariate and multivariate analyses even from one temporal perspective) should be the first step in the development of any wetland management plan. That floc, and to a lesser extent peat, has escaped such characterisation on the Swan Coastal Plain highlights a lack of understanding of key wetland processes, critical, one would have thought, to wetland management. This issue is explored further in Chapter 7.

CHAPTER 4
BIOGEOCHEMICAL EFFECTS OF DRYING, REWETTING AND AERATION ON THE ORGANIC SEDIMENTS OF A PERMANENTLY INUNDATED, ALKALINE LAKE ON THE SWAN COASTAL PLAIN, WESTERN AUSTRALIA

Abstract

This study investigated the (bio-)geochemical effects (with a focus on potential for eutrophication and/or acidification) of drying and oxidation on two types of organic sediments (peat and suspended detrital floc) from a permanently inundated, alkaline wetland on the Swan Coastal Plain, Western Australia. Slurries of dried/rewet and continuously wet sediments of both types were incubated under anaerobic and aerated conditions for 49 days. In the peat drying/rewetting had little effect on phosphorus, sulfur, Fe and Ca transformations under anaerobic conditions. Under aeration however significant amounts of sulfate were released, resulting in considerable decreases in pH, and mobilisation of Ca. Drying 'dampened' the oxidative effects caused by aeration in that significantly less sulfate was released and pH also declined less. In the floc sediment, drying significantly increased total filterable phosphorus (TFP) concentration under both anaerobic and aerated conditions. Alongside the considerable release of TFP in the dried/rewet anaerobic slurries, pH decreased, and [Fe] and [Ca] increased markedly upon rewetting, and recovered only slowly over time. The decrease in pH was interpreted as being due to the accumulation of CO_2 brought about by intense microbial activity, which in turn was spurred on by high nutrient concentrations. As in the peat slurries, aeration increased sulfate mobilisation in the continuously wet floc slurries. However, this was less than half the amount of sulfate released in the peat slurries, and caused only minimal decreases in pH. This was interpreted as possibly being related to the floc structure, to the nature of the sulfides present (e.g. the presence of an iron-sulfide/surface Fe(II)-CO_3 complex), and to high TFP concentrations which may have inhibited sulfur oxidation. As in the peat slurries drying significantly reduced the amount of sulfate released under aerated conditions, however, unlike the peat slurries where pH continued to decline over time, the pH in the aerated floc slurries increased significantly over time. On Day 49 the pH of these slurries was comparatively high

(mean 8.1) and this was speculatatively (because nitrogen species were not measured) interpreted as being largely the result of ammonification, spurred on by drying-induced release of organic nitrogen.

The 'dampening' effect of drying against sediment oxidation was most likely the result of the development of water repellence in both sediment types. This water repellence, known from the soils sciences to be caused by the formation of organic coatings on sediment particles, had significant consequences, both for the retardation of acidification and the exacerbation of eutrophication.

4.1 Introduction

Climate change and increased groundwater abstraction in recent years have caused a number of groundwater dependent wetlands on the Swan Coastal Plain (SCP), Western Australia, to experience lower water levels, shorter periods of inundation and more extreme summer droughts (Sommer & Horwitz, 1999, 2001). This has affected the water quality and ecology of individual wetlands in a number of different, and often contrasting ways. Although much research on the effects of wetting and drying has been carried out on agricultural soils (Bresson & Moran, 1995; Groffman & Tiedje, 1988; Kay & Dexter, 1992; Paul et al., 1999; Phillips & Greenway, 1998; Sparling & Ross, 1988; Sparling et al., 1985; Van Schreven, 1967), rice paddies (Ponnamperuma, 1972, 1984; Ratering & Schnell, 2001) and northern hemisphere wet fens, mires and other wetlands (Carvalho & Moss, 1999; Hughes et al., 1997; Lamers, Tomassen et al., 1998; Lucassen et al., 2002, 2005; Van Haesebroeck, 1997; Venterink et al., 2002), in Australia, comparatively little has been conducted on the sediments of natural lakes, particularly on shallow wetlands, such as the ones prevalent on the SCP. In eastern Australia, Baldwin (1996) and Mitchell & Baldwin (1998) studied the effects of oxidation and drying on the phosphorus dynamics of sediments from a small eutrophic storage dam in New South Whales (Chaffey Dam), and Mitchell & Baldwin (1999) studied the effects of desiccation of sediments from another reservoir (Lake Hume) on nitrification, denitrification and methanogenesis. In Western Australia, Qui & McComb (1994, 1995, 1996) studied the phosphorus and nitrogen dynamics of fresh and air-dried sediments from a shallow, seasonal wetland on the SCP (North Lake). They also investigated the interrelationships between iron extractability and phosphate sorption in reflooded air-dried sediments from a number of shallow lakes south of Perth (Qui & McComb, 2002).

As many of the SCP wetlands continue to dry more often and more severely, local authorities responsible for their management are increasingly being harassed with complaints from nearby residents about malodours, nuisance midge swarms, toxic algal blooms, loss of aesthetic amenity, acidic borewater, etc. Although drying and wetting can have marked, and often irreversible, physical effects on wetland sediments (Bresson & Moran, 1995; Grootjans et al., 1985; Kay & Dexter, 1992; Rajaram & Erbach, 1999; see also review in Chapter 2), the major cause of all of these problems are the biogeochemical changes that take place when wetland sediments dry and then rewet. How these changes manifest themselves will depend on a number of factors, such as: sediment properties (sediment composition, nutrient and organic content); type of drawdown (gravity or evaporative); severity of drying (proportion of drying area, rate of drawdown, degree of dewatering, temperature and time of sediment drying and weathering); and conditions of refilling (origin of water, degree of sediment disturbance) (McComb & Qui, 1998).

Of all of the impacts drying/rewetting of sediments can cause, the effects on nutrient transformations (especially eutrophication potential) and the potential for acidification are the two of most concern. It is generally acknowledged that drying brings about a 'flush of nutrients' upon rewetting which supports increases in primary and bacterial productivity (Baldwin, 1999; McComb and Qui, 1998). The nutrients (primarily phosphorus and nitrogen) originate mainly from the death of microbial biomass, as well as from the breakdown of organic matter and stimulation of microbial activity (Crozier et al., 1995; Frierer & Schimmel, 2002; Qui and McComb, 1995; Soulides & Allison, 1961; Sparling & Ross, 1988; Sparling et al., 1985 and others). In addition, prolonged drying has been associated with an increase in the crystallinity of Fe (oxy-)hydroxides which decreases the sorption capacity of the sediment for phosphorus (Baldwin, 1996; Lijklema, 1980). Aquatic organic sediments are often nutrient-rich and thus particularly susceptible to drying-induced nutrient release.

As so many factors can influence how a sediment will respond to wetting and drying, the opposite finding has also been reported, i.e. that drying and rewetting decreases the amount of dissolved P concentrations in the water column (Haynes & Swift, 1985; Jacoby et al., 1982; Sommer and Horwitz, 2001). Most of the reports on drying-induced decreases in P-availability have dealt with acidic soils/sediments which suggests that the impact of drying on P availability was primarily related to its impact on pH. For example, if drying results in a decrease in soil pH from say, 5.8 to 5, this

will increase the soil's binding capacity for P, either through precipitation with Fe and aluminium oxides, or through increased adsorption onto these oxides (Haynes and Swift, 1985; Holford, 1983; Kopacek et al., 2000; Stumm & Morgan, 1996).

The increases in available N following rewetting have generally been attributed to drying-induced increased mineralization of organic matter, with the amount of N mineralized being directly related to the amount of organic matter present (Davidsson & Stahl, 2000; Grootjans et al., 1985). The increased N mineralization results in an accumulation of ammonium in the sediments which is subsequently released into the overlying water upon rewetting. Qui and McComb (1996), and others, found that in oxygenated water, this flush of ammonium stimulated nitrification. This nitrification then stimulated denitrification in the anaerobic sediments. Denitrification then ultimately leads to the loss of N (as N_2 or N_2O/NO_x gas) from the system. Ponnamperuma (1972) states that alternate wetting and drying increases denitrification loss, while continuous submergence minimizes this, and may even lead to an accumulation of N in the sediments. Hence, McComb and Qui (1998) suggested that drying and reflooding of organic-rich sediments offers potential for nitrogen removal from eutrophic wetlands. In acidic wetlands however, drying-induced acidification may severely impede nitrification Rao & Dutka (1983), leading to potentially large accumulations of ammonium in the water column, particularly if additional NH_4^+ were mobilized from sediment exchange sites (Sommer and Horwitz, 2001).

Drought-induced acidification of wetlands usually occurs when poorly buffered, sulfidic sediments are present (Carvalho and Moss, 1999; Hughes *et al.* 1997; Lamers *et al.* 1998; Lucassen *et al.* 2002). In Western Australia there have been a number of instances in recent years where organic-rich (peaty) wetlands have acidified after drying (the drying often followed by fire, exacerbating the impacts -Horwitz et al., 1999; Horwitz et al., 2003). Organic sediments (peat) are particularly susceptible to acidification upon exposure because they can contain large stores of pyrite. This is especially so for peats that have had some form of marine influence during their paleohistory (Dellwig et al., 2002; Dent & Lawson, 2002). High sulfate input from sea water, combined with high Fe and ample organic matter favour sulfate-reducing bacterial activity, creating conditions that are very conducive to pyrite formation (Giblin & Wieder, 1992). Acidification results from the oxidation of the reduced sulfidic or ferrous minerals (e.g. pyrite) upon rewetting and can have devastating effects on aquatic as well as human ecology (Appleyard et al., 2004).

There are no published Australian studies (to my knowledge*) that have investigated processes associated with drought-induced acidification of shallow, freshwater wetlands, nor any that have investigated the combined potential for acidification and effects on nutrient dynamics of drying and oxidation of organic-rich sediments. Although it is generally acknowledged that the organic status of a sediment will influence a wetland's response to drying/rewetting (McComb and Qui, 1998), the potential role that organic matter plays in drying/wetting related processes appears to have been overlooked by wetland researchers.

This chapter describes an incubation experiment that investigated the geochemical effects of drying and reflooding (under anaerobic and aerated conditions), focussing on the potential for eutrophication and/or acidification, on the organic sediments of a wetland situated in an alkaline catchment on the Swan Coastal Plain, Western Australia. The experiment was designed to enable identification of the overall effects of drying/rewetting and oxidation on the transformations of the important chemical constituents, pH, redox potential, electrical conductivity, Fe, Ca, sulfate and phosphate and from these, infer processes responsible for changes from known relationships between variables (including unmeasured ones).

4.2 Materials and methods

4.2.1 Study site, sample collection and preparation

The study site, sample collection and preparation methodologies have been described in the previous chapter (Chapter 3). A detailed characterisation of the Lake Goollelal sediments is also given in Chapter 3.

4.2.2 Experimental design and incubation methods

The experiment was set up as a multivariate factorial design with repeated measures, having two between-subject factors, 'Treatment' (continuously wet and dried/rewet sediment) and 'Incubation Type' (anaerobic and aerated slurries), and one within-subject variable, 'Time' (sampling days 7, 21, 35 and 49). There were six subjects ('Sites'). The two sediment types being investigated, i.e. 'Peat' and 'Floc', were treated separately. Table 4.2.1 shows the experimental layout.

* although two papers relating to eastern Australia, McCarthy, Conalin, D'Santos, & Baldwin, 2006, and Hall, Baldwin, Rees, & Richardson, 2006, are in press at the time of writing.

Table 4.2.1

Experimental layout

TREATMENT	CONTINUOUSLY WET								DRIED/REWET							
INCUBATION TYPE	ANAEROBIC				AERATED				ANAEROBIC				AERATED			
DAY	7	21	35	49	7	21	35	49	7	21	35	49	7	21	35	49
SITES	6	6	6	6	6	6	6	6	6	6	6	6	6	6	6	6

There were 6 dependent variables: pH, electrical conductivity (EC), Fe, Ca, SO_4^{2-} and total filterable phosphorus (TFP).

The experiment was designed to test the following hypotheses for each of peat and floc:

1. There is no difference in the measured variables between continuously wet and dried/rewet (=treatment type) sediment under anaerobic conditions (=incubation type).
2. There is no difference in the measured variables between continuously wet and dried/rewet (=treatment type) sediment under aerated conditions (=incubation type).
3. For each treatment type and incubation type, there is no difference in the measured variables over time.

Ten grams of air-dried (see Chapter 3) sediment of each type was placed into each of two black 1-L, narrow-necked polyethylene bottles (one for the anaerobic, and one for the aerated treatment). For the continuously wet treatments, wet sediment equivalent to 10 g air-dry weight was also placed into two bottles (this was conducted in an anaerobic glove-box [*Extech Pty Ltd]*). For the dried/rewet treatments 500 ml, and for the continuously wet treatments 500 ml minus the water content of the sediment, of Milli-Q water was then added to the bottles to give a 1:50 sediment to water ratio. For the anaerobic treatments, the Milli-Q water was first de-oxygenated by gently bubbling with ultra-high purity N_2 gas for 60 minutes. The slurries were then suspended by shaking manually. The aerated treatments received air delivered by small polyethylene tubes (2 mm inner diameter) to the bottom of the bottles and were aerated continuously for the entire duration of the experiment. The anaerobic slurries remained sealed at all times, except when physico-chemical measurements and porewater samples were taken,

which was done in the anaerobic chamber. The slurries were kept in a temperature-controlled room at 20°C, and were left to equilibrate overnight. Physico-chemical measurements (temperature, dissolved oxygen, redox potential, pH and EC) were taken on Days 1, 7, 14, 21, 28, 35 and 49 using portable WTW (*Wissenschaftliche Technische Werkstaetten*) multi-meters. On Days 7, 21, 35 and 49, 50 ml porewater samples were extracted with a 60-ml plastic syringe to which a polyethylene tube was attached. The slurries were manually shaken once daily, and were always shaken prior to taking physico-chemical measurements and removing porewater. Porewater samples were filtered through 0.45 μm cellulose acetate filters (pre-soaked in Milli-Q) into 50 ml polycarbonate (*Falcon*) centrifuge tubes. Aliquots of this were analysed for TFP, sulfate and metals. TFP aliquots were frozen until analysis. The sulfate aliquots were preserved with 2-M zinc acetate (Eaton, Clesceri, & Greenberg, 1995) and stored in a cool-room at between 3-4°C until ready for analysis. The aliquots destined for metal analyses were preserved in 2% nitric acid. Chemical analyses are outlined in Section 4.2.3.

Porewater sampling could not remove exactly a 50:1 ratio of water:sediment, and therefore the ratio of water:sediment remaining in the slurries after each sampling session declined (i.e. proportionately more water was being removed than sediment). In addition, more sediment was being removed from the "continuously wet" than from the "dried/rewet" slurries, therefore the "dried/rewet" samples were always (apart from the first week) somewhat more concentrated than the continuously wet samples. To overcome these problems bottles were always weighed before and after taking samples, the difference in weight being the combined weight of water and sediment removed. The dried weight of sediment on filter papers in the centrifuge tubes was measured, allowing measured variables to be adjusted to a standardised 1:50 sediment:ratio. For EC, metal, phosphate and sulfate, this was achieved linearly (e.g. a reading of 300 μS cm^{-1} at a ratio of 45:1 was adjusted to 270 μS cm^{-1}). pH was first converted to $[H^+]$, then this was also linearly adjusted, before converting back to pH. It was assumed that for pH below 7 concentration results in a decline in pH (since the $[H^+]$ is higher in the concentrated sample), for pH above 7 concentration of a sample would result in a rise in pH (because the $[OH^-]$ is greater in the concentrated sample) (Thomas, 1996). It is acknowledged that in reality this is not quite so straightforward because of buffering effects from the sediment. However, because it requires a 10x dilution/concentration to increase/decrease the pH by 1 unit, the changes in pH due to these adjustments were generally very small. For example, a pH of 5.00 at a ratio of 46:1 was adjusted to 5.04, and a pH of 8.00 at the same ratio was converted to 7.96. Furthermore, in order to

compensate for evaporation in the aerated treatments, an amount of Milli-Q water equivalent to the difference in weight of the bottles at the end of the previous sampling session to the beginning of the next was added to the slurries after each sampling session.

4.2.3 Chemical analyses

4.2.3.1 Total Filterable Phosphorus

Sample vials become exposed to air immediately upon opening and this has the potential to change the concentration of filterable reactive phosphorus, particularly through precipitation with Fe. For this reason samples were digested with ammonium persulfate in an autoclave (Eaton et al., 1995) before appropriate dilution and analysing colourimetrically on a *SKALAR* autoanalyser using the ascorbic acid method (Eaton et al., 1995). In the remainder of this chapter the term 'Total Filterable Phosphorus' (TFP) will be used to refer to this fraction.

4.2.3.2 Sulfate

Treatment with $ZnCH_3COO$ and NaOH resulted in samples with very high pH (~12.5) and total dissolved solids (~3,600 mg L^{-1}). Capillary electrophoresis proved to be an efficient method of dealing with such samples when the chromate-based electrolyte buffer described below is used. A *Waters Quanta 4000 Capillary Electrophoresis System* equipped with a reversible-polarity power supply was used for sulfate analysis. A fused silica capillary (600-mm by 76-μm i.d.) was used to separate anions. The detection window was located approximately 535 mm from the injection point of the capillary. Ultraviolet detection was carried out at 254 nm. Sample introduction was by hydrostatic injection. Sample time was 5 seconds, run time 4.5 minutes, and the capillary run voltage was set at 25 kV, at a temperature of 25 °C. Migration time for sulfate was generally around 2.5 (+/- 0.5) minutes. Standard solutions of 10, 20, 50, 75 and 100 mg L^{-1} SO_4^{2-} were prepared by dissolving appropriate amounts of analytical-grade Na_2SO_4 in Milli-Q water. The calibration curves used for quantitative analysis were linear over the concentration range covered (typically $r^2 > 0.98$). The electrolyte buffer solution was prepared by combining 5 mM chromic acid (H_2CrO_4), 20 mM diethanolamine (DEA) and 5 mM tetradecytrimethyl-ammonium bromide (TTAB). TTAB was added to reverse the electro-osmotic flow, so that the anions migrated in the direction of the detector, resulting in fast analysis times. pH of the buffer solution was 9.2. Chromic acid, rather than sodium chromate was used

in order to get a more stable baseline and to avoid system peaks due to the presence of sodium ions. Between each sample the capillary was flushed with buffer for 2 minutes. Fresh buffer was used after each run of 20 samples. The electropherograms were recorded and processed with *Varian Star* software.

4.2.3.3 Metals

Metals were analysed by atomic absorption spectroscopy (AAS) on a *Varian* flame AAS. Iron and manganese were determined at a wavelength of 248.3 and 279.5 respectively using an oxidizing air-acetylene flame, and a lamp current of 5 mA. Calcium and Al were determined at a wavelength of 422.7 and 309.3 respectively using a reducing nitrous oxide-acetylene flame, and a lamp current of 10 mA. In order to suppress ionization of Ca and Al, more readily ionizable potassium (as KCl) was added to samples and standards to achieve a concentration of 0.2%. Standards were prepared from commercial elemental stock solutions of 1000 mg L^{-1} (*Australian Chemical Reagents*). Because there was not enough sample available to carry out all four analyses (and initially, arsenic and copper were also going to be analysed), samples were diluted (5x). Unfortunately this reduced the concentration of Al and Mn to at or below detection limits and these elements are therefore not included in the results of this study.

4.2.4 Statistical analyses

Various ANOVAs (one-way, two-way univariate and repeated measures) on appropriately transformed data were carried out using SPSS vs. 11.0 for Windows to test the hypotheses outlined in Section 4.2.3. Analysis of the data in a single procedure as laid out in Table 4.2.1 could not be performed (i.e. a repeated measures MANOVA in SPSS), mainly because interpretation of the results in such a complex design would have been difficult. In addition, multivariate ANOVAs (MANOVAs) could not be performed because of the low number of subjects, as well as multicollinearity issues between the variables (Zar, 1999). Analyses of covariance (ANCOVAs) were performed to test whether geographical position on the lake was influencing any of the dependent variables. Relationships between variables were tested using Spearman's rank order correlation. Correlation-based principal component analyses (using Primer Package v. 5) were used to summarise patterns of (normalised) elemental distribution and treatment effects (i.e. continuously wet/dried rewet; anaerobic/aerated).

In some instances the parametric analysis of variance assumptions of normality and homoscedasticity could not be met regardless of various transformation attempts. In these cases non-parametric analysis of variance was used (i.e. Kruskall-Wallis test for

one-way, and Friedman's test for repeated measures analysis of variance). In addition, a one-way ANOVA was carried out in order to test the significance of the differences in water:sediment ratios between continuously wet and dried/rewet treatments.

4.3 Results

A one-way ANOVA showed no significant differences ($p>0.05$) in the water:sediment ratios in the 4 treatments (using combined peat and floc data) until Day 49 (Appendix table 4.1a). A Tukey's post-hoc test (Appendix table 4.1b) indicated that on Day 49 the difference was due to ratio differences between the dried/rewet and the continuously wet treatments (and not between anaerobic and aerated treatments). By Day 49 the continuously wet treatments had become statistically significantly ($p<0.05$) more dilute than the dry treatments.

During the course of the experiment, particularly towards the end, the Site 6 aerated samples (both peat treatments, but only the continuously wet floc) had much lower pH values than the other sites (although trends were the same). The Site 6 samples that were kept anaerobic behaved in a similar manner to the other sites, although the pH of Site 6 was consistently lower. Analyses of covariance (ANCOVAs) for both the peat and the floc sediments using 'site' (a surrogate for geographical location) as a covariant were non-significant ($p>0.05$). However, on Day 7 pH, Day21 TFP and Day 49 pH and TFP were significant ($p<0.05$) unless Site 6 was removed. Therefore, where the Site 6 data were not in line with the rest of the data, results are presented for Sites 1-5 only.

4.3.1 Peat

4.3.1.1 D.O. and ORP

Dissolved oxygen in the aerated treatments was maintained above 4.5 mg L^{-1}, and there was a trend of increasing oxygen concentrations over time (Fig 4.3.1). In the anaerobic treatments, D.O. was always < 0.08 mg L^{-1}. ORP in the aerated treatments ranged from 70 to 235 mV (Fig. 4.3.2), while in the anaerobic treatments ORP increased during the first two weeks, then decreased over time (range 14 to -220 mV). These latter measurements are, however, somewhat unreliable, as stable potentials could not be attained (i.e. the readings on the meter never settled properly), so that ORP had to be estimated over a range of values. This could have been due to 'slow redox equilibrium (low exchange currents)', 'mixed potentials' (i.e. redox partners are not in equilibrium with each other, or the potentials are a composite of two or more processes), or fouling

of the Pt electrode with PtS (Stumm and Morgan, 1996). There is considerable controversy regarding the justification of measuring redox potentials in aquatic systems. For example, Thorstenson (1984) stated that, based on thermodynamic data, hydrated electrons could not exist at physically meaningful equilibrium concentrations under natural conditions, and therefore could not be measured in natural waters. The odour from the samples, however, clearly indicated anaerobic conditions.

4.3.1.2 pH

pH movements over time are shown in Figure 4.3.3. The mean pH in the anaerobic dried/rewet treatments was lower on Day 1 than the continuously wet samples (6.43 vs. 6.95, n=5; 1-way ANOVA [Kruskall-Wallis], $p<0.001$). However, the pH of the continuously wet samples declined somewhat over time, and on Day 49 it was 0.28 units lower than on Day 1. In contrast, the pH of the dried and rewet samples increased over time, and on Day 49 it was 0.36 units higher than on Day 1. From Day 21 onwards, there were no statistically significant differences in pH between the continuously wet and the dried/rewet anaerobic slurries, and by Day 49 the pH in both treatments was identical.

Aeration also had the effect of lowering the mean pH of the continuously wet samples on Day 1, when compared to the anaerobic samples (6.48 vs. 6.95, n=5; $p<0.05$). The pH of the aerated continuously wet samples declined more significantly over time (by 1.50 pH units) than did that of the continuously wet anaerobic samples (only 0.15 units). Drying initially made no difference to the pH of the aerated samples (both 6.4 on Day 1). However, over time the pH of the continuously wet aerated samples declined more than did the pH of the dried/rewet aerated samples (mean of 4.98 vs. 5.61 on Day 49). The changes in pH over time were overall statistically significant, and were also significant between treatment types and between incubation types (all $p<0.001$, see Repeated Measures ANOVA Table 4.3.1).The differences in pH between continuously wet and dried/rewet samples on individual days were significant ($p<0.05$) only on Days 21 and 35, while the differences in pH between anaerobic and aerated samples were significant on all four days (Table 4.3.2).

4.3.1.3 EC

Figure 4.3.4 is roughly a mirror image of Figure 4.3.3. It shows that, as with pH, aeration had a much stronger effect on the EC of the peat samples than did drying. Whereas the EC of both anaerobic treatments (continuously wet and dried/rewet) remained more or less steady throughout the incubation period (mean between 290 and 353 $\mu S\ cm^{-1}$), EC of the aerated samples continued to rise until Day 49. Drying had no marked effect on the EC of the peat sediment under anaerobic conditions. When samples were aerated, however, the EC of the dried/rewet peat was consistently lower than that of the continuously wet peat**.** A Kruskall-Wallis test showed that this difference was statistically significant only from Days 14 onwards (Days 21-35 $p<0.01$; Day 49 $p<0.05$). These observations are further reflected in the Repeated Measures analyses (Tables 4.3.1 and 4.3.2). Overall, the change in EC over time was significant, the EC over time between continuously wet and dried/rewet samples was significant, as was the change in EC over time between anaerobic and aerated samples (all $p<0.001$). Two-way univariate tests (Table 4.3.2) showed that the differences in EC between continuously wet and dried/rewet samples were not significant on any of the days, while the differences in EC between anaerobic and aerated samples were significant on the last three days only ($p<0.001$).

4.3.1.4 Iron

Dissolved Fe as concentration ($mg\ L^{-1}$) and as percentage of total sediment Fe (2^{nd} y-axis; see Chapter 3) over time are shown in Figure 4.3.5. The most striking feature of this graph, apart from its 'noisiness' is the extremely low amounts of Fe released. The large error bars are probably due to the E-W gradient in sediment Fe content within the lake (see Chapter 3). In the anaerobic treatments, drying and rewetting appeared to decrease the mean [Fe] on Day 7 (1.14 mg L^{-1} vs. 2.62 mg L^{-1}, or 0.45% vs. 0.24% of total Fe respectively; n=5), however, this was not statistically significant. In the continuously wet anaerobic slurries [Fe] slightly decreased, while in the dried/rewet anaerobic samples it slightly increased over time. However, the difference between the two anaerobic treatments was not significant on any of the days, and on Day 49 [Fe] was nearly the same (1.95 vs. 2.08 mg L^{-1} or 0.38% vs. 0.40% of total Fe respectively).

Aeration had the effect of decreasing [Fe] of the continuously wet slurries when compared to the anaerobic slurries, however this was statistically significant only on Day 49 ($p<0.05$). Drying initially decreased the amount of Fe released in the aerated

samples (0.34 mg L^{-1} vs. 1.03 mg L^{-1}, or 0.08% vs. 0.20% of total Fe respectively), however, again this was not statistically significant, and by Day 49 [Fe] in both treatments was nearly the same (continuously wet aerated: 0.22 mg L^{-1} [0.05%], dried/rewet aerated: 0.33 mg L^{-1} [0.08%]). The Repeated Measures analyses (Table 4.3.1) show that the only significant effect was the change in [Fe] over time between aerated and anaerobic samples. The Two-way ANOVA (Table 4.3.2) shows that the difference in [Fe] was significant only between the anaerobic and aerated (continuously wet and dried/rewet samples combined) samples on Days 7 and 49.

4.3.1.5 Calcium

Figure 4.3.6 shows the changes in dissolved Ca over time as concentration (mg L^{-1}) and as percentage of total sediment Ca (secondary y-axis) for the four treatment groups. Calcium concentration in the continuously wet anaerobic bottles remained relatively constant throughout the sampling period (15-16 mg L^{-1}; ~5% of total sediment Ca), and drying had no pronounced effect on these (15-17 mg L^{-1}). Aeration however significantly increased [Ca] on all days (15-16 mg L^{-1} vs. 27-91 mg L^{-1}, n=5, all $p<0.01$; see Table 4.3.2), and there was an increasing trend over time which showed no sign of stabilising on Day 49. The mean amount of Ca released until Day 49 in the continuously wet aerated bottles represented only 34% of total sediment Ca; or 26% if Site 6 is omitted. Calcium concentration in the aerated dried/rewet treatments was lower than in the aerated continuously wet samples (1-way ANOVAS at least $p<0.01$ on all days), but higher than those in the anaerobic treatments (1-way ANOVAs days 21 ($p<0.05$), 35 ($p<0.01$), and 49 ($p<0.001$)). The changes (i.e. increases) in [Ca] over time between incubation types ($p<0.001$) and between treatment types ($p<0.05$) were significant (see Table 4.3.1).

4.3.1.6 Sulfate

Sulfate movements over time are shown in Figure 4.3.7. In the anaerobic treatments, drying and rewetting significantly increased [SO_4^{2-}] on Day 7 (mean 42 mg L^{-1} vs. 24 mg L^{-1} (n=6; $p<0.01$). However, this decreased over time, and by Day 49 the situation had reversed; i.e. the mean [SO_4^{2-}] in the continuously wet anaerobic samples was higher than that of the dried/rewet samples (27 mg L^{-1} vs. 45 mg L^{-1}, $p<0.05$). The differences between the two anaerobic treatments were not significant on Days 21 and 35. As would be expected, aeration significantly increased [SO_4^{2-}] of the continuously wet samples on all of the sampling days (mean 24 mg L^{-1} to 45 mg L^{-1} in the anaerobic treatments vs. 104 mg L^{-1} to 342 mg L^{-1} in the aerated treatments; all $p<0.001$). Drying

decreased the amount of SO_4^{2-} released in the aerated samples on all of the sampling days by ~40% (all at least $p<0.05$), and there was an increasing trend over time in both treatments. Temporal changes in $[SO_4^{2-}]$ were overall significant, and were also significant between incubation types and between treatment types (all $p<0.001$; see Table 4.3.1). The difference in $[SO_4^{2-}]$ between the anaerobic and aerated (both treatments combined) samples was highly significant on all days (all $p<0.001$; see Table 4.3.2). The difference in $[SO_4^{2-}]$ between continuously wet and dried/rewet samples (both incubation types combined) was significant on Days 21, 35 and 49 (all $p<0.01$; Table 4.3.2), but not on Day 7.

4.3.1.7 Total Filterable Phosphorus (TFP)

Total filterable P movements over time are shown in Figure 4.3.8 as concentration ($\mu g\ L^{-1}$) and as percentage of total sediment phosphorus. The large error bars are a reflection of the spatial pattern in sediment phosphorus content within the lake (see Chapter 3). In the anaerobic treatments, drying and rewetting increased TFP concentrations on all of the days (continuously wet anaerobic: 227 to 274 $\mu g\ L^{-1}$ [3.26 to

Table 4.3.1

Repeated Measures ANOVA table for the dependent variables pH, EC, Fe, Ca, SO_4^{2-}, and TFP in the peat treatments. All variables apart from pH were log-transformed. For pH and Fe, n=5, the rest n=6. The degrees of freedom were corrected using the Huynh-Feldt measure because sphericity assumptions were violated for all variables except TFP. For TFP sphericity was assumed. (F computed using alpha 0.05; * $p<0.05$; ** $p<0.01$; *** $p<0.001$; ns= not significant)

	df	pH	EC	Fe	Ca	SO_4^{2-}	TFP
(df)		2.35	2.35	2.34	2.38	2.37	3
Within-Subjects							
Day		51.171**	64.584**	2.899 ns	49.048**	40.957***	0.294 ns
Day*Treatment		9.065***	7.655**	3.061 ns	4.784*	11.132***	0.885 ns
Day*Incubation		58.81***	44.819**	6.398**	60.511**	22.403***	3.934**
Day*Treatment* Incubation Type		0.723 ns	4.51*	1.347 ns	2.359 ns	8.787***	0.364 ns
Between-Subjects							
Treatment	1	3.304 ns	3.438 ns	0.633 ns	9.163**	8.358**	0.219 ns
Incubation Type	1	40.66***	37.994**	3.794 ns	74.693**	120.095***	18.319**
Treatment* Incubation Type	1	4.97*	5.123*	0.028 ns	11.929**	3.327 ns	2.057 ns

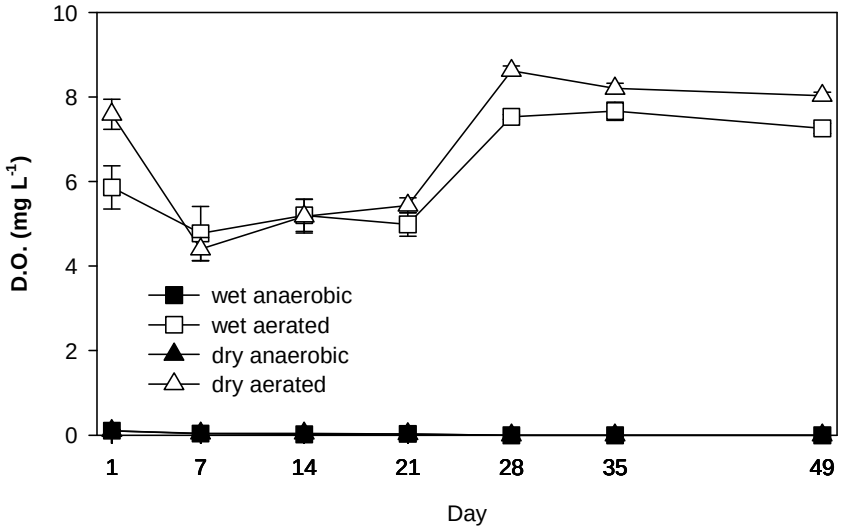


Figure 4.3.1: Dissolved oxygen concentration over time for each of the four treatment combinations in the peat slurries. (n=6; error bars are standard errors)

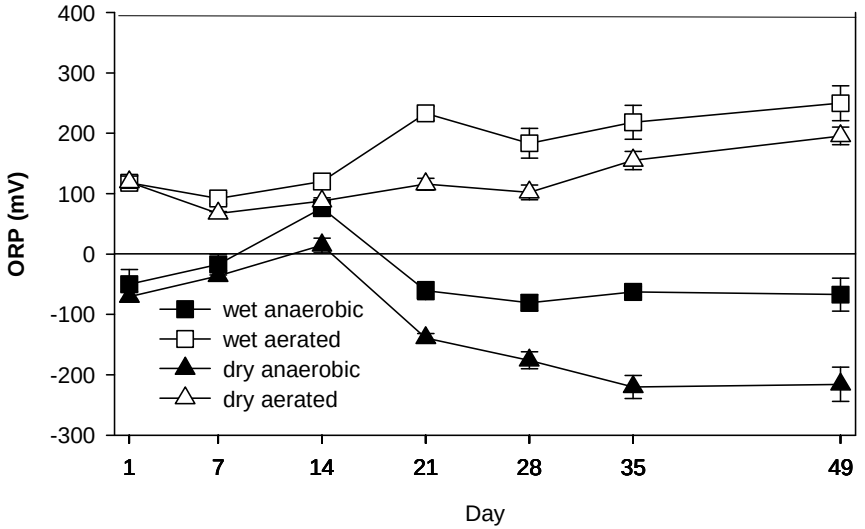


Figure 4.3.2: Redox potential (ORP) over time for each of the four treatment combinations in the peat slurries. (n=6; error bars are standard errors)

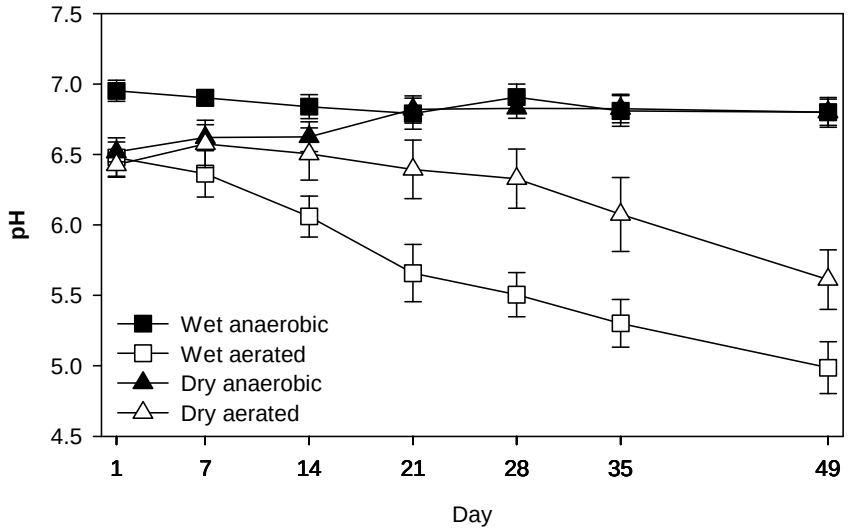


Figure 4.3.3: pH over time for each of the four treatment combinations in the peat slurries. (n=5; error bars are standard errors)

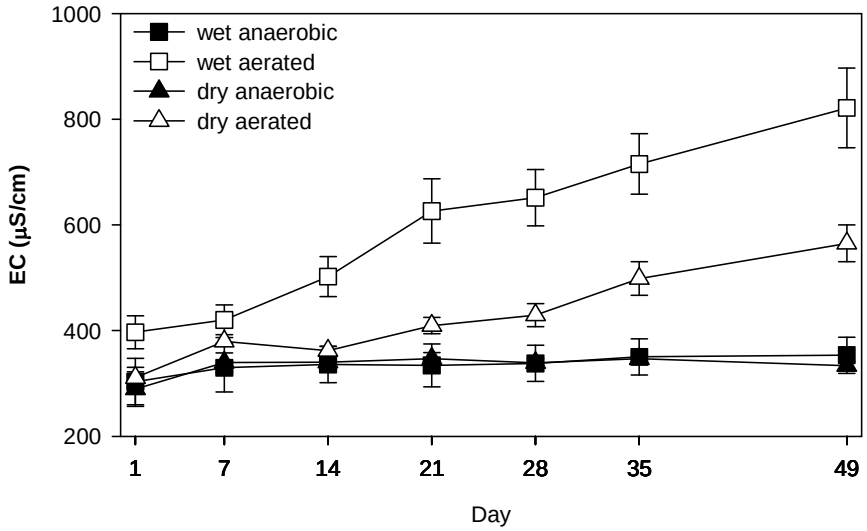


Figure 4.3.4: Electrical conductivity measurements over time for each of the four treatment combinations in the peat slurries. (n=6; error bars are standard errors)

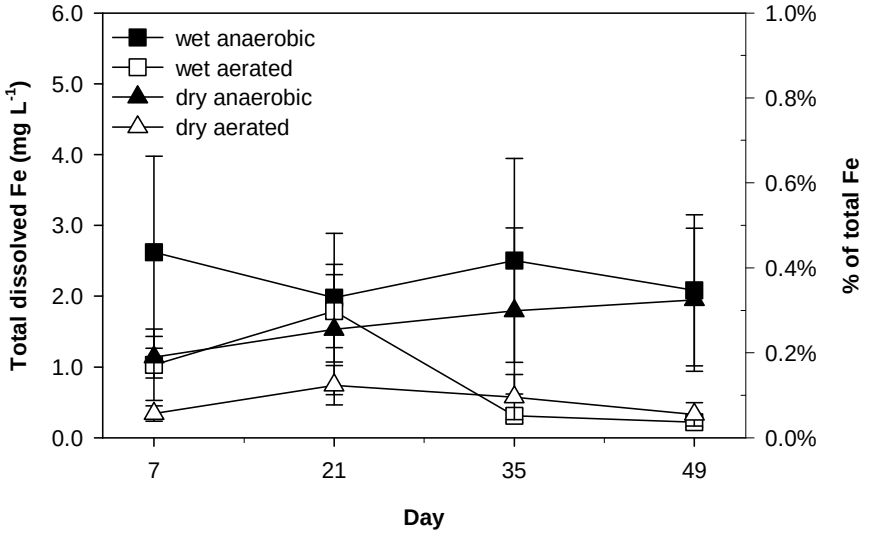


Figure 4.3.5: Dissolved iron concentration over time for each of the four treatment combinations in the peat slurries. Secondary y-axis=Percentage of total sediment iron released. (n=5; error bars are standard errors)

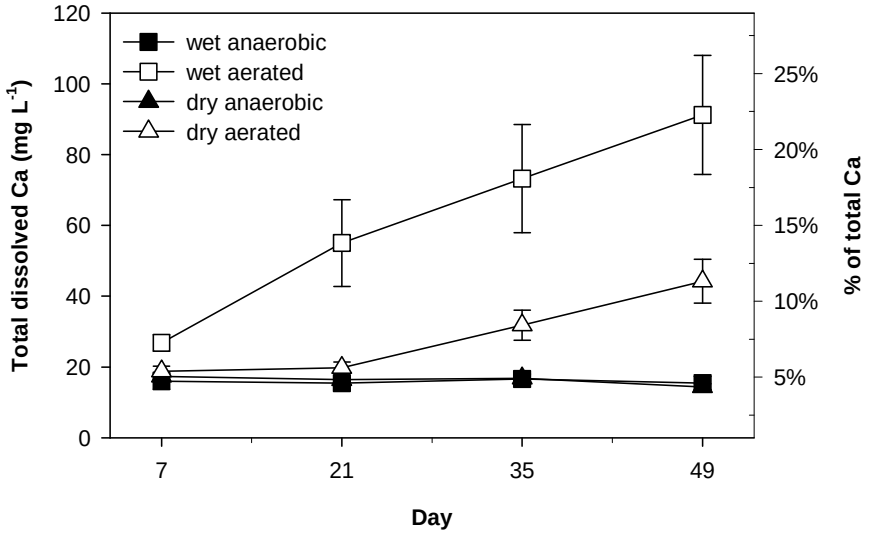


Figure 4.3.6: Dissolved calcium concentration over time for each of the four treatment combinations in the peat slurries. Secondary y-axis= Percentage of total sediment calcium released. (n=6; error bars are standard errors)

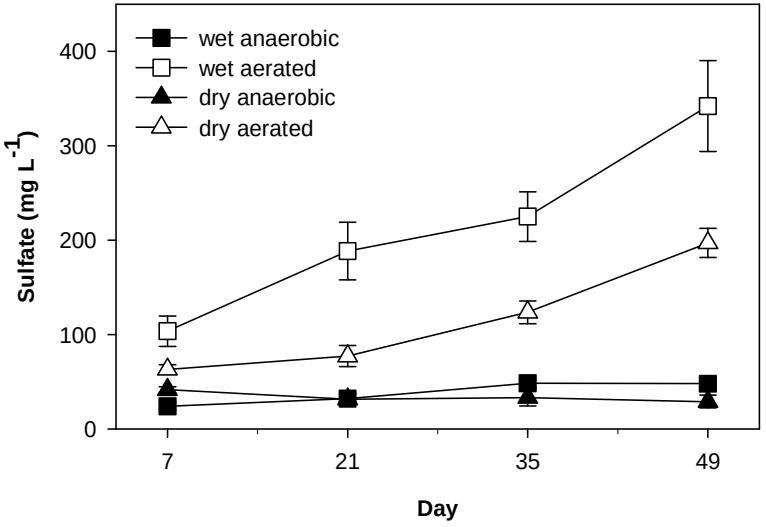


Figure 4.3.7: Sulfate concentration over time for each of the four treatment combinations in the peat slurries. (n=6; error bars are standard errors).

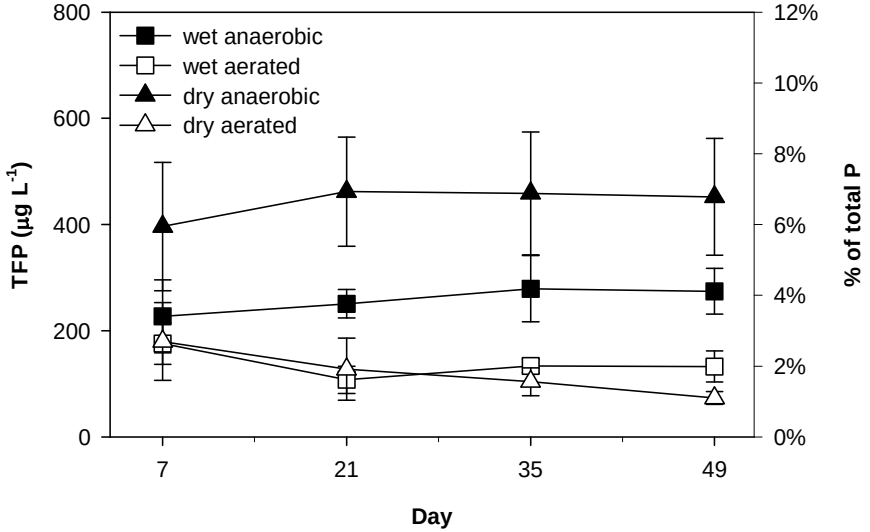


Figure 4.3.8: Total filterable phosphorus concentration over time for each of the four treatment combinations in the peat slurries. Z-axis=% total sediment P released (n=6; error bars are standard errors**)**

Table 4.3.2

Univariate two-way ANOVAs (peat treatments) testing the significance of the differences in the independent variables pH, EC, Fe, Ca, SO_4^{2-} and TFP between treatments on individual sampling days. All variables apart from pH were log-transformed. (F computed using alpha 0.05; *p<0.05; **p<0.01; ***p<0.001; ns= not significant)

	PH (n=5)				**EC** (n=6)				**Fe** (n=5)			
Day	7	21	35	49	7	21	35	49	7	21	35	49
Levene's Test	1.795 ns	0.708 ns	3.248 ns	2.871 ns	7.681***	6.709**	5.281**	4.014*	1.099 ns	1.889 ns	3.151 ns	2.848 ns
Treatment	0.073 ns	5.517*	5.208*	3.984 ns	0.018 ns	4.448*	5.370*	6.489*	2.999 ns	1.517 ns	0.039 ns	0.004 ns
Incubation Type	5.045*	22.822***	42.836***	91.623***	5.742*	25.596***	53.249***	76.968***	5.376*	0.059 ns	3.494 ns	10.369**
Treatment* Incubation Type	3.635 ns	4.686*	4.793*	3.984 ns	0.967 ns	8.979**	6.259*	4.466*	0.015 ns	0.185 ns	0.436 ns	0.059 ns
	Ca (n=6)				**SO_4^{2-}**(n=6)				**TFP** (n=6)			
Day	7	21	35	49	7	21	35	49	7	21	35	49
Levene's Test	2.773 ns	0.517 ns	0.194 ns	0.711 ns	0.945 ns	0.336 ns	1.507 ns	2.927 ns	0.052 ns	1.033 ns	1.692 ns	1.627 ns
Treatment	1.482 ns	13.231**	8.799**	8.992**	0.349 ns	7.996**	14.279***	12.606**	0.443 ns	0.894 ns	0.000 ns	0.096 ns
Incubation Type	12.761**	43.534***	78.870***	131.501***	49.073***	57.436***	105.568***	163.393***	2.390 ns	17.222***	13.928***	30.979***
Treatment* Incubation Type	6.411*	18.409***	9.556**	6.804*	15.033***	5.659*	0.150 ns	0.062 ns	1.116 ns	0.342 ns	2.142 ns	3.849 ns

3.65% of total sediment P] vs. dried/rewet anaerobic: 396 to 452 μg L^{-1} [5.63 to 6.65% of total P]), although this was not statistically significant on any of the sampling days (1-way ANOVAs). In both treatments the trend was slightly increasing between Days 7 and 35, and then stabilizing between Days 35 and 49 (temporal variation was not significant). Aeration decreased the amount of TFP in the continuously wet samples on all of the days (continuously wet anaerobic: 227 to 274 μg L^{-1}, continuously wet aerated: 176 to 133 μg L^{-1}), this difference being significant on Days 21 ($p<0.01$), 35 and 49 (both $p<0.05$), but not on Day 7. On Days 7 and 21 the TFP concentration in both aerated treatments were similar, and on Days 35 and 49 there was less (statistically non-significant) TFP in the dried aerated than in the continuously wet aerated treatment (104 μg L^{-1}/73 μg L^{-1} vs. 134 μg L^{-1} and 133 μg L^{-1} respectively).

4.3.1.8 The peat 'big picture'

Figure 4.3.9 shows the ordination resulting from a PCA analysis using all variables and Days 7, 21, 35 and 49 (Sites 1-5). Most (92.5%) of the total variation in the data could be explained by the first two principal components. All variables were relatively equally weighted in the outcome of the PCA. The graph clearly shows the more important role of incubation type, compared to treatment, with the aerated samples loosely grouped on the right side, and the anaerobic slurries tightly grouped to the lower left side of the graph. Within the aerated groups there are distinct temporal patterns, a reflection primarily of the gradually increasing [SO_4^{2-}], [Ca] and EC, and decreasing pH over time (see Figures 4.3.1-4.3.8). Within the anaerobic samples a temporal pattern is less obvious. Further well presented is the separation of wet and dried/rewet slurries within the aerated treatments. Again, within the anaerobic treatments this is less obvious.

After agglomeration of the log-transformed and standardised data using Euclidean distance, an analysis of similarity (2-way crossed ANOSIM in Primer) revealed significant differences between incubation types (global R:0.875, $p< 0.003$). Wet and dried/rewet samples were also significantly different, although less so than between incubation types (global R: 0.266, $p< 0.05$).

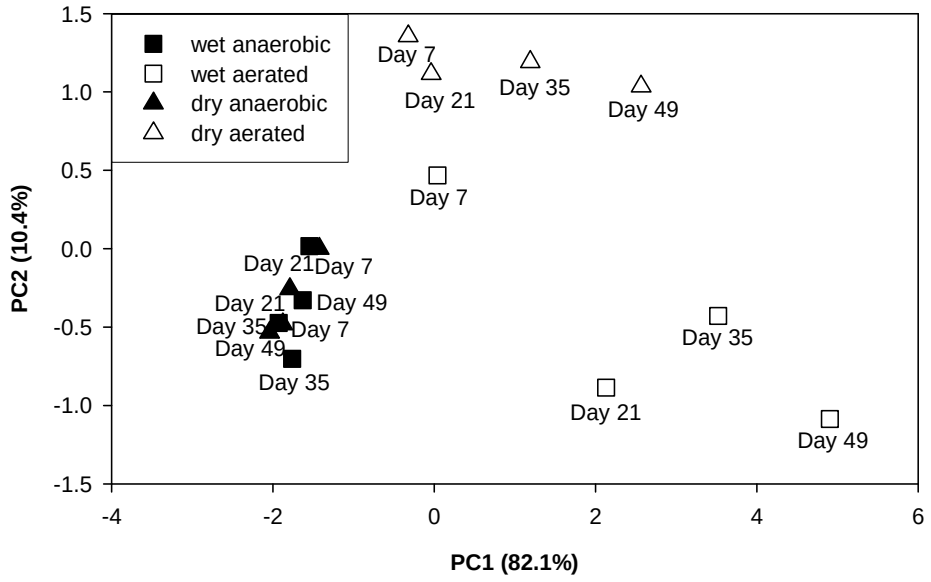


Figure 4.3.9: Two-dimensional PCA ordination of the standardised incubation data using all variables, and Days 7, 21, 35 and 49 (Sites 1-5). PC1 and PC2 account for 92.5% of the total variability.

4.3.2 Floc

4.3.2.1 D.O. and ORP

It was not possible to reliably measure dissolved oxygen in the floc slurries because the fine, flocculant nature of this sediment type (i.e. much of it remained in suspension) kept clogging the oxygen probe. As mentioned in Section 4.3.1.1, ORP measurements also posed problems, particularly in the anaerobic treatments. Floc ORP movements are shown in Appendix 4.4 as an indication only. In the first two weeks, the dried/rewet floc slurries emitted an overpoweringly unpleasant odour, from both the anaerobic and the aerated treatments (although much stronger in the anaerobic treatment). These odours appeared different to typical 'rotten egg gas' smell and gradually decreased over time. The dried and ground floc sediment had a distinctive greeny/grey colour and 'herbaceous' odour, very unlike the peat samples, which were dark brown and simply smelled 'peaty'.

4.3.2.2 pH

pH movements over time are shown in Figure 4.3.10. In the anaerobic treatments, drying and rewetting substantially lowered the mean pH of the floc when

compared to the continuously wet samples (Day 1 5.69 vs. 7.08, n=5; Kruskall-Wallis asympt. significance: $p<0.01$ on Days 1-35). Whilst the pH of the continuously wet samples remained relatively constant over time, the pH of the dried/rewet anaerobic samples increased throughout the incubation period, and on Day 49 the difference between continuously wet and dried/rewet anaerobic treatments was no longer statistically significant (continuously wet anaerobic: 7.06, dried/rewet anaerobic: 6.83). In contrast to the peat incubations, aeration had virtually no effect on the pH of the continuously wet floc samples (both had pH's around neutral throughout the incubation period). Drying initially decreased the mean pH of the aerated samples (Day 1: continuously wet aerated pH 7.05, dried/rewet aerated pH 6.17, n=5, Kruskall-Wallis asympt. significance: $p<0.01$). On Day 7 the pH of both the continuously wet and dried/rewet aerated samples were identical (6.97), and then the pH of the dried/rewet aerated samples continued to rise until Day 49 (up to pH 8.11). The difference in pH between the continuously wet aerated and the dried/rewet aerated samples was significant from Days 21 to 49 (Kruskall-Wallis asympt. significance: $p<0.01$).

Temporal changes in pH were significant overall, and also between treatment and incubation types (all $p<0.001$; see Repeated Measures ANOVA Table 4.3.3). The differences in pH between continuously wet and dried/rewet samples were significant (at least $p<0.05$) on all days except Day 35, while the differences in pH between anaerobic and aerated samples were significant on all four days (all $p<0.001$; see Table 4.3.4). The interaction between treatment and incubation type was also highly significant ($p<0.001$) on all four days.

4.3.2.3 EC

Electrical conductivity in the continuously wet anaerobic treatment did not fluctuate much over time (654 to 707 μS cm^{-1}; Figure 4.3.11). Drying/rewetting significantly increased EC in the anaerobic treatments on each of the 7 sampling days (1-way ANOVAs, n=5, all $p<0.001$), and there was a marked increasing trend over time, apart from Day 49 when EC declined slightly from 2213 μS cm^{-1} to 1630 μS cm^{-1}. Aeration had little effect on the EC of the continuously wet samples. As with the anaerobic samples, drying/rewetting had the effect of increasing the EC of the aerated samples, although not as drastically as in the continuously wet ones (continuously wet aerated EC: 609-766μS cm^{-1}; dried/rewet aerated EC: 1035-1308

μS cm^{-1}). This was statistically significant on all 7 sampling days (1-way ANOVAs, n=5, all $p<0.01$).

A Repeated Measures ANOVA could not be performed for EC because the data could not be normalized (i.e. Box's M test was significant even on variously transformed data). However, a non-parametric Friedman test indicated that, overall, there were significant differences in EC over time (n=5, $p<0.01$; looking at Figure 4.3.11 it is obvious that this statistic was mainly influenced by the dried/rewet treatments).

4.3.2.4 Iron

As in the peat slurries, very little Fe was present in any of the floc incubations (Figure 4.3.12). Negligible amounts of Fe were released in the continuously wet anaerobic slurries (ranging from 0.00 on Day 35 to 0.65 mg L^{-1} [or 0.11% of total sediment Fe] on Day 7). Drying/rewetting markedly increased this, although there was a decreasing trend over time (3.15 mg L^{-1} on Day 7 to 1.05 mg L^{-1} on Day 49, or 0.53% to 0.18% of total sediment Fe). Kruskall-Wallis one-way tests (n=5) indicate that the difference in dissolved [Fe] between the continuously wet anaerobic and dried/rewet anaerobic treatments was significant from Days 7 to 35 (all $p<0.01$), but not on Day 49. Aeration decreased the amount of Fe released from the continuously wet sediment on Day 7 (0.13 mg L^{-1} vs. 0.65 mg L^{-1}, Kruskall-Wallis $p<0.01$), however on Day 21 there was more Fe in the aerated (0.26 mg L^{-1}) than in the anaerobic (0.02 mg L^{-1}) bottles (and this, too, was significant $p<0.01$). On Day 35 both incubation types had below detection limits [Fe] in all of the bottles, and on Day 49 the continuously wet aerated treatment again had slightly less Fe (0.14 mg L^{-1}) than the continuously wet anaerobic treatment (0.31 mg L^{-1}). Drying/rewetting had the effect of slightly increasing the amount of Fe released from the aerated samples (statistically significant only on Day 7 (0.81 mg L^{-1} vs. 0.13 mg L^{-1}, Kruskall-Wallis $p<0.05$)).

4.3.2.5 Calcium

The mean [Ca] in the continuously wet anaerobic treatment remained relatively stable over time (56 mg L^{-1} on Day 7 to 51 mg L^{-1} on Day 49 (equivalent to ~13.8% – 12.6% of total sediment Ca, see Figure 4.3.13). Unlike the peat samples, and similar to the response of Fe, drying/rewetting markedly increased the

amount of Ca released in the anaerobic treatments (1-way ANOVAs, n=5, Days 7-21: $p<0.01$; Day 49: $p<0.05$), and there was a decreasing trend over time (from 154 mg L^{-1} [~38% of total sediment Ca] on Day 7 to 121 mg L^{-1} [~30% of total sediment Ca] on Day 49). Aeration also increased Ca release in the continuously wet slurries, (continuously wet anaerobic: 51 mg L^{-1} to 56 mg L^{-1}; continuously wet aerated: 67 mg L^{-1} to 79 mg L^{-1}); and there was an increasing temporal trend. In the aerated slurries, drying/rewetting initially increased Ca release (by 28 mg L^{-1} on Day 7). On Day 21 [Ca] in the aerated continuously wet and dried/rewet treatments was identical (67 mg L^{-1}), and on Days 35 and 49 it was higher in the continuously wet than in the dried/rewet samples. This resulted in the one-way ANOVAs for all days being not significant. Calcium movements over time were only significant between treatment types ($p<0.01$; see Table 4.3.3).

4.3.2.6 Sulfate

Sulfate movements over time are shown in Figure 4.3.14. In the anaerobic treatments, there was slightly more SO_4^{2-} in the dried/rewet than in the continuously wet treatments on Day 7 (mean 31 mg L^{-1} vs. 20 mg L^{-1}, n=5). However, this decreased over time, and on Days 35 and 49 the situation had reversed; i.e. the mean [SO_4^{2-}] in the continuously wet anaerobic samples was slightly higher than that in the dried/rewet samples (mean 9 mg L^{-1} vs. 1 mg L^{-1}). Aeration significantly increased [SO_4^{2-}] in the continuously wet samples on all of the sampling days (mean range 0 mg L^{-1} to 20 mg L^{-1} in the anaerobic treatments vs. 82 mg L^{-1} to 168 mg L^{-1} in the aerated treatments; all $p<0.001$). Drying/rewetting decreased the amount of SO_4^{2-} released in the aerated samples on all of the sampling days by ~50% (although statistically significant only on Day 35, $p<0.05$), and there was an increasing trend over time in both treatments (continuously wet aerated samples: 82 to 168 mg L^{-1}; dried/rewet aerated samples: 40 – 62 mg L^{-1}). The changes in [SO_4^{2-}] over time were significant overall, and were also significant between treatment and incubation types (all $p<0.01$; see Table 4.3.3). The two-way ANOVAs (Table 4.3.4) show that the difference in [SO_4^{2-}] between continuously wet and dried/rewet samples was significant on Days 35 and 49 (all $p<0.01$), but not on Days 7 and 21. The difference in [SO_4^{2-}] between the anaerobic and aerated (continuously wet and dried/rewet samples combined) samples was highly significant on all days (all $p<0.001$).

Table 4.3.3

Repeated Measures ANOVA table for the dependent variables pH, Fe, Ca, SO_4^{2-} and TFP in the floc incubations. Ca, SO_4^{2-} and TFP were log-transformed. Iron was reciprocally transformed. The degrees of freedom were corrected using the Huynh-Feldt measure because sphericity assumptions were violated for all variables except TFP. For TFP sphericity was assumed. (F computed using alpha 0.05; * p<0.05; **p<0.01; ***p<0.001; ns= not significant; n=5)

	df	**pH**	**Fe**	**Ca**	**SO_4^{2-}**	**TFP**
(df)		2.26	2.041	1.954	1.711	3
Within-Subjects						
Day		31.913***	22.352***	13.080***	8.904**	21.759***
Day*Treatment		25.183***	4.754*	9.112**	7.174**	13.647***
Day*Incubation Type		2.456 ns	3.986*	1.609 ns	16.576***	1.239 ns
Day*Treatment* Incubation Type		3.637*	7.197**	3.362*	3.353 ns	2.860*
Between-Subjects						
Treatment	1	2.108*	23.684***	8.285**	19.817***	886.654**
Incubation Type	1	40.112***	11.064**	2.640 ns	180.827***	2.822 ns
Treatment* Incubation Type	1	45.898***	5.805*	9.555**	0.052 ns	5.050*

4.3.2.7 Total Filterable Phosphorus (TFP)

Total filterable P movements over time are shown in Figure 4.3.15. In the anaerobic treatments, drying and rewetting increased TFP concentrations on all of the sampling days by many orders of magnitude (continuously wet anaerobic: mean range 22 to 99 μg L^{-1} [or 0.04-0.21% of total P] vs. dried/rewet anaerobic: 18103 to 35635 μg L^{-1} [or 37-73% of total sediment P]). In both treatments the trend was more or less decreasing over time. As with EC, aeration had a negligible effect on TFP concentration of the continuously wet samples. These were slightly lower in the continuously wet aerated slurries on Days 7 and 49, while on Days 21 and 35 there was slightly more TFP in the continuously wet aerated than in the continuously wet anaerobic slurries. As in the anaerobic slurries, drying/rewetting very significantly

Table 4.3.4:

Univariate two-way ANOVAs testing the significance of the differences in the independent variables pH, EC, Ca, SO_4^{2-} and TFP between treatments on individual sampling days (floc incubations). All variables apart from pH were log-transformed. (F computed using alpha 0.05; *p<0.05; **p<0.01; ***p<0.001; ns= not significant)

	pH (n=5)				**EC** (n=5)				**Ca** (n=5)			
Day	7	21	35	49	7	21	35	49	7	21	35	49
Levene's Test	1.618 ns	1.742 ns	22.384***	2.455 ns	0.487 ns	1.489 ns	1.610 ns	3.029 ns	0.954 ns	0.787 ns	2.263 ns	8.272**
Treatment	23.678***	5.033*	0.507 ns	16.510***	161.585***	157.872***	147.263***	33.875***	26.100***	9.875**	8.571**	1.038 ns
Incubation Type	21.712***	22.952***	33.757***	40.340***	1.768 ns	6.030*	4.083 ns	0.032 ns	1.181 ns	4.837*	4.010 ns	1.315 ns
Treatment* Incubation Type	23.370***	34.388***	34.971***	39.840***	1.600 ns	11.267**	15.445***	10.849**	6.128*	10.438**	14.794***	6.442*
	SO_4^{2-} (n=5)				**TFP** (n=5)							
Day	7	21	35	49	7	21	35	49				
Levene's Test	0.885 ns	5.283**	2.698 ns	1.285 ns	1.671 ns	0.811 ns	5.313**	5.100**				
Treatment	0.035 ns	0.749 ns	45.277***	17.755***	961.000***	452.628***	630.876***	114.522**				
Incubation Type	19.347***	41.838***	168.984***	114.632***	9.254**	1.267 ns	0.628 ns	4.335 ns				
Treatment* Incubation Type	9.407**	0.780 ns	2.633 ns	1.685 ns	0.035 ns	3.703 ns	4.506*	4.796*				

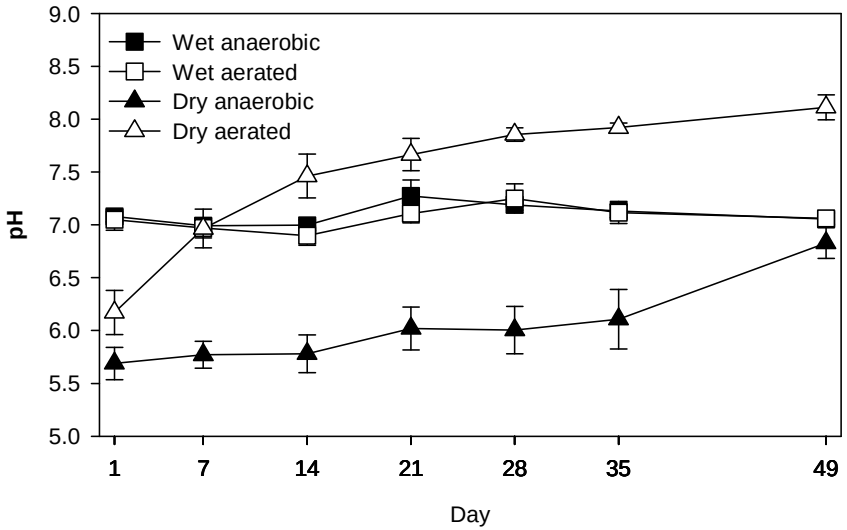


Figure 4.3.10: pH over time for each of the four treatment combinations in the floc slurries. (n=5; error bars are standard errors)

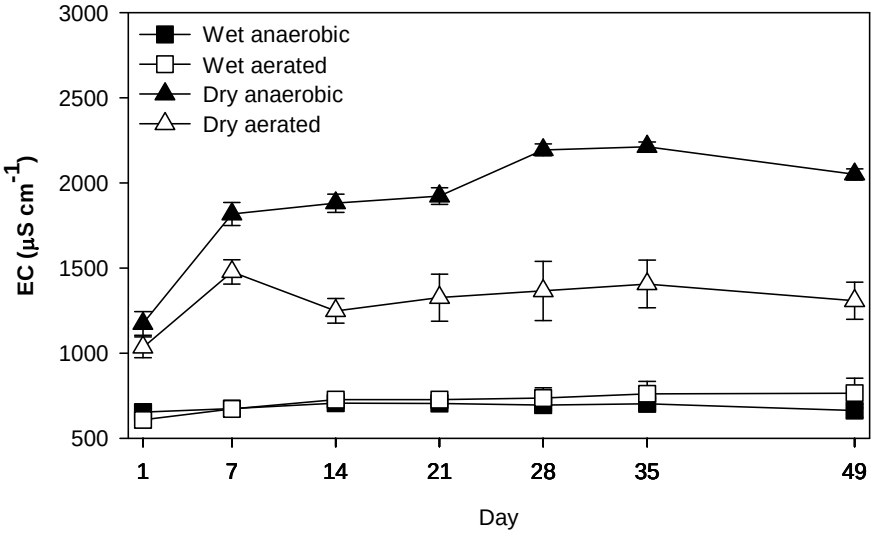


Figure 4.3.11: EC over time for each of the four treatment combinations in the floc slurries. (n=5; error bars are standard errors)

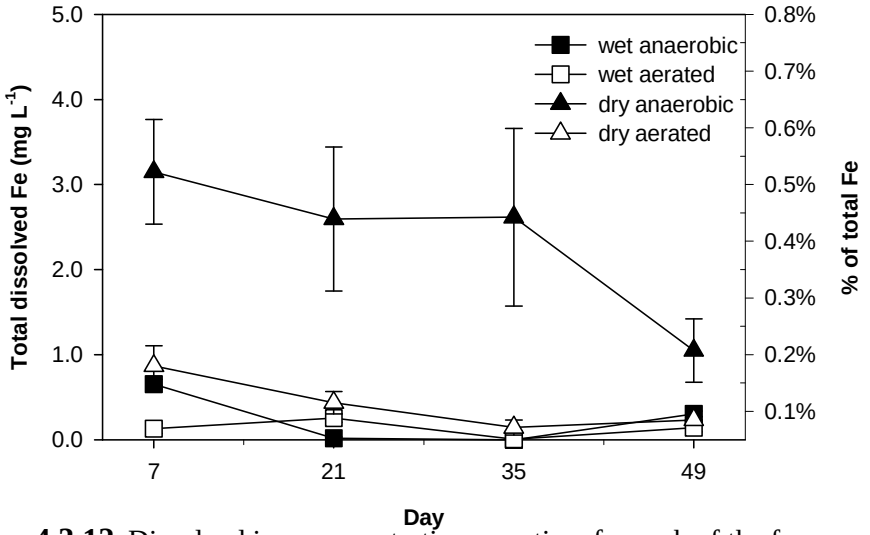


Figure 4.3.12: Dissolved iron concentration over time for each of the four treatment combinations in the floc slurries. Secondary y-axis=% of total sediment iron released. (n=5; error bars are standard errors)

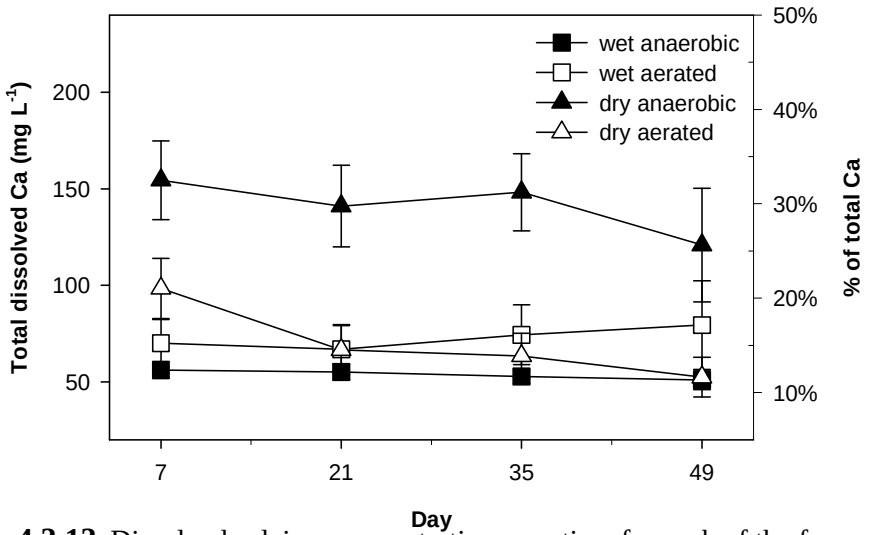


Figure 4.3.13: Dissolved calcium concentration over time for each of the four treatment combinations in the floc slurries. Secondary y-axis=% of total sediment calcium released. (n=5; error bars are standard errors)

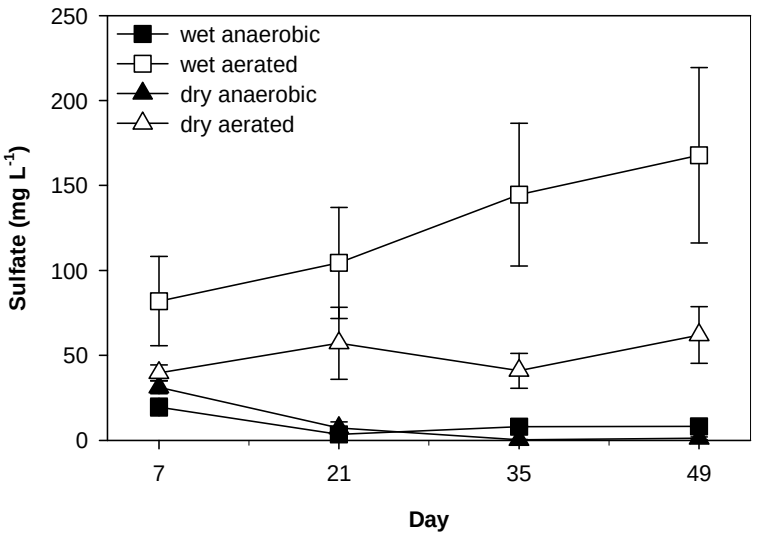


Figure 4.3.14: Sulfate concentration over time for each of the four treatment combinations in the floc slurries. (n=5; error bars are standard errors)

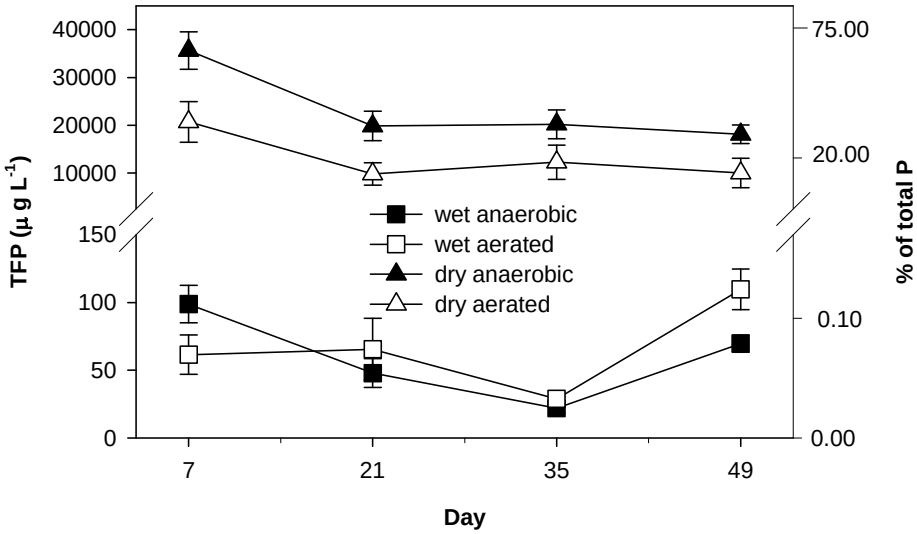


Figure 4.3.15: Total filterable phosphorus concentration over time for each of the four treatment combinations in the floc slurries. Secondary y-axis=% of total sediment P released. (n=5; error bars are standard errors)

increased the amount of TFP in the aerated slurries (mean range continuously wet aerated: 29 μg L^{-1} to 65 μg L^{-1} [or 0.06-0.14% of total P]; dried/rewet aerated: 9788 μg L^{-1} to 20705 μg L^{-1} [or 18.9-40.7% of total P]; all $p<0.001$, n=5). Also as in the dried/rewet anaerobic treatment, there was a decreasing trend over time. Overall, the changes in TFP over time were significant ($p<0.01$; Table 4.3.3), the difference in TFP changes over time between continuously wet and dried/rewet slurries was also significant ($p<0.01$), but the difference in TFP changes over time between anaerobic and aerated samples was not significant. The difference in TFP between continuously wet and dried/rewet samples was highly significant on all of the sampling days (all $p<0.001$). The difference in TFP between anaerobic and aerated samples was significant only on Day 7 ($p<0.01$; Table 4.3.4).

4.3.2.8 The floc 'big picture'

Figure 4.3.16 shows the ordination resulting from a PCA analysis using all variables and Days 7, 21, 35 and 49 (Sites 1-5). 85.2% of the total variation in the data could be explained by the first two principal components. All variables were relatively equally weighted in the outcome of the PCA. In contrast to the peat, where the groupings were based primarily on incubation type, in the floc the clusters appear to be primarily based on treatment. This is a reflection of the overriding role that

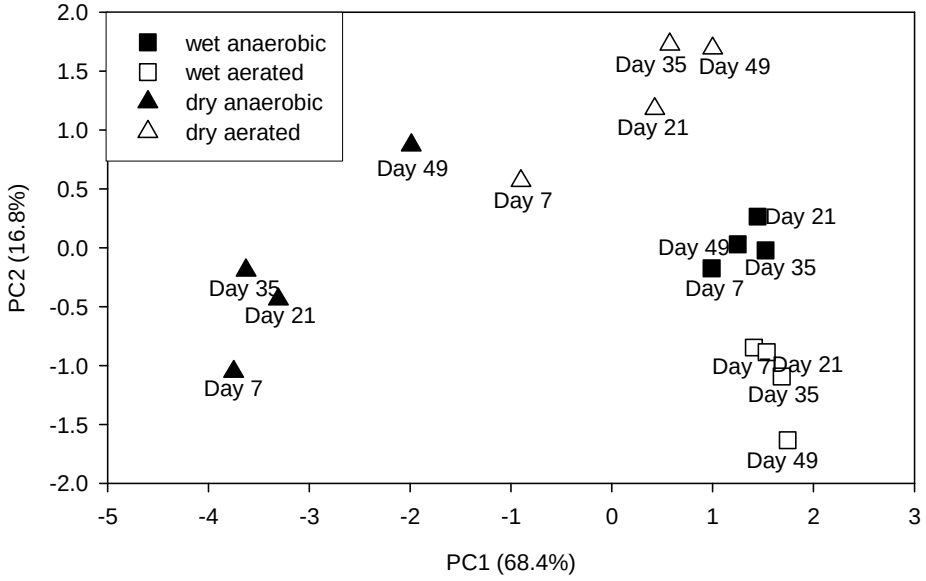


Figure 4.3.16: Two-dimensional PCA ordination of the standardised incubation data using all variables, and Days 7, 21, 35 and 49 (Sites 1-5). PC1 and PC2 account for 85.2% of the total variability.

drying plays over incubation type. However, each of the groups also show distinct clusters of their own, reflecting the distinct impact of each of the treatment and incubation combinations on the floc.

After agglomeration of the log-transformed and standardised data using Euclidean distance, an analysis of similarity (2-way crossed ANOSIM in Primer) revealed highly significant differences between treatment types (global R:0.974, $p<0.001$). Anaerobic and aerated samples were also significantly different, although less so than between treatment types (global R: 0.573, $p< 0.003$).

4.3.3 Comparison of sediment types

Table 4.3.5 gives an overview of the responses of the peat and floc sediments to drying/rewetting and aeration. The table shows that the main differences between the peat and floc were the effect of drying/rewetting (without aeration) on pH (peat: no significant effect; floc: significant decrease), EC (peat: no significant effect; floc: significant increase), calcium (peat: no effect; floc: significant increase), and TFP (peat: slight increase; floc: substantial increase). Other notable differences were the effect of aeration on the pH of the continuously wet samples (peat: significant decrease; floc: no effect), and the effect of drying on the pH of the aerated samples (peat: decline over time; floc: significant increase over time).

The PCA ordination in Figure 4.3.17 displays the patterns described in Table 4.3.1. PC1 which explains 48.3% of the variation in the data, was mainly influenced by TFP and EC (i.e. decreasing along the X-axis), while PC2 (which explained 27.3% of the variation in the data) was mainly influenced by pH and SO_4^{2-} (i.e. decreasing pH and increasing SO_4^{2-} downwards along the Y-axis). The peat anaerobic samples group together tightly, reflecting the minor impact that drying had on the peat sediment under anaerobic conditions. The floc continuously wet anaerobic samples also cluster closely to the peat anaerobic groups, a reflection of the relative geochemical stability of the (undried) floc under anaerobic conditions. The effect of aeration on the continuously wet peat is also apparent. These samples form a separate loose cluster, becoming more different from anaerobic peat over time (i.e. decreasing pH and increasing $[SO_4^{2-}]$ over time, in effect perpetual acidification). The dry aerated peat samples form another loose cluster (showing the

Table 4.3.5:

Comparison of peat and floc responses to drying and aeration

Variable	Treatment	Peat	Floc
pH	Mean range over all treatments	4.70 – 6.85	5.69 – 8.12
	Drying without aeration	Initial decrease; then no significant difference.	Also decrease, but much greater than that of peat; increasing over time but still significantly lower than continuously wet samples.
	Aeration without drying	Decline and continued decline over time to mean 4.70.	No effect.
	Drying and aeration	Initially no effect; then decline over time but less than in continuously wet aerated.	Initial decline; then significant rise over time (to mean 8.12)
EC	Mean range over all treatments	289 to 821 µS cm^{-1}	610 – 2095 µS cm^{-1}
	Drying without aeration	Steady in both anaerobic treatments; no significant effect.	Marked increase and increasing trend over time (to mean 2095 µS cm^{-1}).
	Aeration without drying	Significant increase, and increasing over time (to mean 821 µS cm^{-1}).	Slight initial increase, then no difference.
	Drying and aeration	Lower than aeration alone (but still higher than anaerobic treatments).	Significant increase, but not as high as dried anaerobic (to mean 1332 µS cm^{-1}).
Iron	Mean range over all treatments	0.30 – 2.62 mg L^{-1}	0 – 4.30 mg L^{-1}
	Drying without aeration	No significant effect.	Initial significant increase, then decreasing trend over time.
	Aeration without drying	Slight decrease.	Initial decrease then similar conc. As anaerobic (all low).
	Drying and aeration	Initial decrease, then same as continuously wet aerated.	Initial significant increase, then only slightly more than continuously wet aerated.

Variable	Treatment	Peat	Floc
Calcium	Mean range over all treatments	14 – 94 mg L^{-1}	46 – 150 mg L-1
	Drying without aeration	No effect.	Significant increase with decreasing trend over time.
	Aeration without drying	Significant increase, and increasing over time.	Slight increase with increasing trend over time.
	Drying and aeration	Lower than aeration alone (but higher than anaerobic treatments.	Initial slight increase compared to continuously wet aerated, then no significant difference.
Sulfate	Mean range over all treatments	24 – 342 mg L^{-1}	0 – 190 mg L^{-1}
	Drying without aeration	Initial significant increase, then decreasing trend, and significantly more in continuously wet anaerobic treatment.	No significant effect.
	Aeration without drying	Significatn increase, and increasing over time.	Significant increase, and increasing over time.
	Drying and aeration	Lower than aeration alone (but higher than anaerobic treatments.	Lower than aeration alone (but higher than anaerobic treatments.
TFP	Mean range over all treatments	73 – 462 µg L^{-1}	25 – 37897 µg L^{-1}
	Drying without aeration	Higher on all days (although statistically insignificant), with initial increasing trend, then stabilization.	Substantial increase, with decreasing trend over time in both anaerobic treatments.
	Aeration without drying	Significant decrease.	No significant effect.
	Drying and aeration	No significant difference between continuously wet aerated and dried aerated.	Substantial increase, but not as high as dried anaerobic.

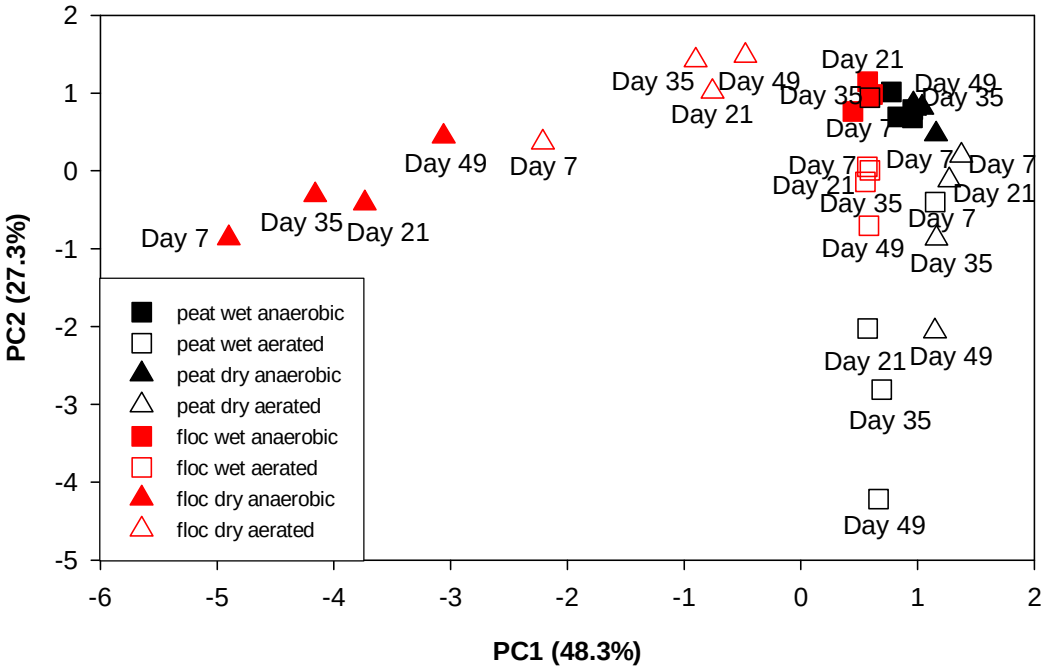


Figure 4.3.17: Two-dimensional PCA ordination of the standardised incubation data for both sediment types (peat and floc) using all variables, and Days 7, 21, 35 and 49 (Sites 1-5). PC1 and PC2 account for 75.6% of the total variability.

same temporal trend), however this is not as removed from the anaerobic peat clusters as the continuously wet aerated peat (a reflection of the 'dampening' effect that drying had on the peat). The anaerobic dried floc samples form the most removed group, a manifestation of the substantial TFP concentration in these samples. This cluster is also loose, showing some sort of recovery over time (i.e. moving closer to the continuously wet anaerobic floc cluster). The dried aerated floc samples form a similarly loose cluster to the dried anaerobic floc; however this is closer to the continuously wet floc samples than the dried anaerobic peat. This is a reflection of the fact that considerable amounts of TFP were also released in aerated dried floc incubations, although not as marked as in the dried anaerobic floc. The relatively minimal impact of aeration on the continuously wet floc samples is reflected in the proximity of this cluster (which also shows a small temporal trend towards increasing [SO_4^{2-}]) to the continuously wet anaerobic floc cluster.

After agglomeration of the log-transformed and standardised data using Euclidean distance, an analysis of similarity (1-way ANOSIM in Primer) revealed that there were highly significant differences between sediment types (global R: 0.359, $p < 0.001$). This justifies the separate treatment of the two sediment types in this thesis.

4.4 Discussion

4.4.1 Peat

Some comments on D.O. and ORP

The recorded redox potentials (E_h or ORP) in the aerated peat slurries (Figure 4.3.2) are relatively low compared to those indicated by Ponnamperuma (1972, 1984) as being typical of oxygenated lake and ocean muds (0.3 to 0.5 V). However reported redox values for the same types of environmental conditions do vary considerably (Stumm & Morgan, 1996). Temperature and amount and type of organic matter are but two of the many factors that influence ORP. The observed increases in ORP over time are probably, at least in part, a reflection of the increased solubility of oxygen over time (Figure 4.3.1). The rate of oxygen solubility in this experiment may have been increased if a diffuser stone could have been fitted to the tubes delivering the oxygen, however it was feared that these would clog up with the fine sediment, hence they were not used. Only from Day 28 onwards did the dissolved oxygen concentration in the aerated peat slurries approach 100% saturation. Despite the difficulties encountered in measuring the ORP of the anaerobic slurries (see section 3.1), the observed pattern of an initial rise in ORP before decreasing asymptotically with time (Figure 4.3.2) is similar to that described by Ponnamperuma (1972; 1984). He suggested that this initial rise is due to the buffering effects of Mn(IV) and Fe(III) oxide hydrates. Although, as mentioned in section 3.1, of limited reliability, Figure 4.3.2 suggests that drying/rewetting in both aerated and anaerobic treatments had the effect of decreasing ORP and in the anaerobic treatment, this became more marked over time. The most likely explanation for this is that the nutrients released as a result of drying spurred on microbial decomposition of organic matter, resulting in lower ORP values.

4.4.1.1 Effects of drying/rewetting under anaerobic conditions

Compared to the continuously wet anaerobic slurries, the dried/rewet anaerobic slurries had lower pH, similar EC, lower [Fe], similar [Ca], slightly higher [SO_4^{2-}] and higher TFP concentration upon rewetting. After 49 days, ORP was lower in the dried/rewet treatment, the pH of both treatments was identical, EC was still similar, [Fe] and [Ca] were similar, [SO_4^{2-}] was slightly lower in the dried/rewet treatment, and TFP was still higher in the dried/rewet treatment.

The most likely reason for the initial lower pH in the dried/rewet anaerobic slurries is the accumulation of CO_2 caused by bacterial respiration upon reinundation. The accumulation of CO_2 has been shown to significantly influence the pH of alkaline

soils in particular, but also organic soils high in Fe, under anaerobic conditions (Ponnamperuma, 1972). Numerous studies from the soil sciences have related increased CO_2 production rates to the rapid rewetting of a dry soil (e.g. Fierer & Schimel, 2002; Soulides & Allison, 1961). Apparently this pulse of CO_2 persists for ~2-6 days. Ponnamperuma (1972) states that the subsequent increase in pH is due to soil reduction and associated consumption of H^+. Oxidation of reduced sulfur may also have been a contributing factor in the initial pH decline. Statistically speaking however the correlation between pH and SO_4^{2-} was only significant on Days 35 and 49. It may come as a surprise that any SO_4^{2-} was present at all when ORP was in the sulfate-reducing range. Giblin & Wieder (1992) maintain that it is not uncommon for SO_4^{2-} to be present in water-logged soils, even at depth. Rewetting of the previously oxidised and dried peat would have released some SO_4^{2-} and H^+ ions causing the pH to fall. Maher, Sullivan, & Ward (2004) also found that the common soil pre-treatment of drying and grinding increased water-soluble SO_4^{2-}. The 'recovery' of the pH to the same level as in the continuously wet slurries occurred between 14 and 21 days after reinundation. This coincided with the ORP in the dried/rewet anaerobic slurries having approached the sulfate-reducing range (mean ~150 mV) on Day 21. On Day 21 the pH and [SO_4^{2-}] of both the continuously wet and the dried/rewet slurries were identical. This relatively slow rate of sulfate reduction is typical in acidic soils/sediments, and according to Ponnamperuma (1972) can be spread out over several months. Given the highly organic nature of the peat, at least part of the 'recovery' of pH in the dried anaerobic treatment may also have been due to buffering by organic matter itself. Organic acids (i.e. their anions) can accept protons and hence buffer pH (Fillion, Probst, & Probst, 1998, 1999). This is further discussed in section 4.4.2.

The most commonly reported physical effect of drying on Fe (hydr/oxides) is an increase in crystallinity upon drying, thereby decreasing solubility, and reducing its future ability to adsorb environmentally important ions such as phosphate (Baldwin, 1996a; McLaughlin et al., 1981; Lijklema, 1980; McLaughlin et al., 1981; Qui & McComb, 2002). This could partially explain why more dissolved Fe (albeit statistically insignificantly) was measured in the continuously wet than in the dried/rewet slurries. However, the findings presented in Chapters 5 and 6 showed that there was no increase in Fe crystallinity. Chapters 5 and 6 moreover showed that less 'adsorbed/exchangeable/carbonate-bound' Fe could be extracted from dried than from undried peat, and this could partially be the reason (the other likely reason is the initial lower pH in the dried/rewet slurries) for the initial lower concentration of Fe in the

dried/rewet, than in the continuously wet anaerobic slurries. Adsorption of organic substances (e.g. humic and fulvic acids) onto Fe (hydr-) oxide surfaces during drying could be the mechanism responsible. This mechanism has been widely reported in the soil sciences literature (e.g. Dekker, Ritsema, Oostindie, & Boersma, 1998; Dekker, Oostindie, & Ritsema, 2005; Doerr et al., 2000; Morley et al., 2005), but not to date in the aquatic sciences. The fact that Fe concentration increased in the dried/rewet anaerobic slurries over time may imply the re-dissolution of these organic coatings, which would also have facilitated subsequent electron transfer after rewetting, and enhanced further reductive dissolution (Stumm, 1997). By Day 49, both treatments had released a mean of only ~0.40% of the total amount of Fe in the slurries. Therefore, regardless of whether the sediment was previously dried or not, the majority of the Fe present remained in insoluble form.

The very low incidence of Fe(hydr-)oxide minerals (Chapter 6) suggests that the higher (although not statistically significant on any of the days) TFP concentrations in the dried/rewet compared to the continuously wet anaerobic slurries was probably more likely to be primarily the direct result of the breakdown of organic matter and the death of microbes (Qui and McComb, 1995; Sparling et al., 1985), than processes related to drying-induced Fe transformations. It must be borne in mind here that TFP (which was measured on digested filtered samples) may well contain considerable amounts of dissolved organic phosphorus. In addition, because of the concomitant drying-induced release of dissolved organic matter (DOC) there would have been competition between phosphate and DOC for sorption sites (mechanisms reviewed in Guppy, Menzies, Moody, & Blamey, 2005), thus retaining P in solution in the short term.

Although there was slightly more Ca dissolved in the dried/rewet than in the continuously wet slurries on Days 7 and 21 (presumably due to the initially lower pH in the dried/rewet slurries), the mean [Ca] in both treatments were identical on Days 35 and 49. At the pH ranges measured in both the continuously wet and the dried/rewet anaerobic slurries (i.e. mean 6.5 – 6.9) phosphate release is unlikely to have been controlled by Ca, since phosphate would be either dissolved, or bound to Fe oxides (Stumm and Morgan, 1996). On Day 49, the mean [Ca] in both slurries was 15 mg L^{-1} (only 4.45% of the total sediment Ca). The high sediment organic matter could have been partially responsible for the lower than expected [Ca] in the anaerobic treatments. Wetzel (2001) states that adsorption of organic compounds to $CaCO_3$ lowers the rates of dissolution in hypolimnetic strata of reduced pH.

4.4.1.2 Effects of aeration vs. effects of drying/rewetting under aerated conditions

Compared to the continuously wet anaerobic incubations, the continuously wet aerated incubations had much higher ORP, lower pH, higher EC, lower Fe, much higher Ca and SO_4^{2-} and lower TFP concentration upon rewetting. These differences were all by and large statistically significant, and tended to become more pronounced over time. By comparison, the dried/rewet slurries had lower ORP, higher pH, lower EC, lower Ca and SO_4^{2-}, but similarly low TFP concentrations than the continuously wet slurries under aerated conditions. For the first three weeks (until Day 21) [Fe] in the continuously wet aerated slurries were higher than in the dried/rewet-aerated slurries, however on Days 35 and 49 they were similarly low.

The major processes operating in the aerated treatments are more easily interpretable than those of the anaerobic treatments. In essence, aeration oxidised reduced sulfur compounds (organic sulfur, and/or FeS or FeS_2), with 92% of the decreases in pH over time being attributable to increases in [SO_4^{2-}] (see correlation tables in Appendix 4.3). The low pH has then led to dissolution of Ca minerals. Increases in SO_4^{2-} and Ca over time in both aerated treatments were strongly reflected in the measured EC's (r^2 all between 0.92 and 1.00), suggesting that these were indeed the dominant processes. Drying/rewetting appears to have significantly 'dampened' the oxidative effects of aeration. This 'dampening' effect of drying was strongly suspected to be due to something blocking the oxidation of the sediment (i.e. probably organic coatings as discussed in 4.4.1.1), and therefore air-dried sediment sub-samples from the same sites were subjected to a standard water-repellence test (Molarity of Ethanol Droplet, see Chapter 3). This test indeed revealed that the dried peat was severely water repellent. In the non-wetting soils literature, water repellence has been typically attributed to the presence of hydrophobic organic substances forming a coating over the surface of soil particles. In aquatic sediments, these organic coatings may block the adsorption of oxygen onto the mineral surfaces under aerated conditions, thus preventing or at least delaying, oxidation (Stumm, 1997).

Why was there more Fe in the continuously wet aerated than in the dried/rewet aerated slurries on Days 7 and 21? When one considers the series of reactions governing pyrite oxidation (summarised by Singer & Stumm, 1970),

$$FeS_2 + 7/2O_2 + H_2O \rightarrow Fe^{2+} + 2SO_4^{2-} + 2H^+ \quad (4.1)$$

$$Fe^{2+} + ¼O_2 + H^+ \rightarrow Fe^{3+} + ½H_2O \quad (4.2)$$

$$Fe^{3+} + 3H_2O \rightarrow Fe(OH)_{3(s)} + 3H^+ \quad (4.3)$$

$$FeS_2+14Fe^{3+}+8\ H_2O \rightarrow 15Fe^{2+} + 2SO_4+16H^+ \qquad (4.4)$$

one can see that in the first reaction dissolved Fe^{2+} and acidity are generated, and in the second dissolved Fe^{3+}. This second step is the rate-limiting step and is slower than the others by some orders of magnitude (much slower than the 49 days' duration of the present experiment; Singer & Stumm, 1970). Only in the third step is ferric Fe hydrolysed and precipitated as $Fe(OH)_3$, generating more acidity in the process. The oxygen in the SO_4^{2-} formed in the first reaction comes mainly from water, not from molecular oxygen (Lowson, 1982; Taylor et al., 1984 in Luther & Church, 1992), suggesting that if a sediment is quickly dried (such as was the case in this experiment), oxidation of pyrite would be limited during the drying process. The fourth reaction occurs as pH decreases and the solubility of Fe^{3+} increases, potentially perpetuating the cycle of pyrite oxidation. The higher [Fe] measured in the continuously wet aerated slurries could be Fe^{2+} produced via the first reaction above, but there could also have been some Fe^{3+}, given the pH values (Day 7 mean in the continuously wet aerated slurries [n=5] 6.3, Day 21, 5.6). Sullivan & Bush (2004) found that in coastal acid sulfate landscapes in eastern Australia acidity (resulting from equation 4.1) was stored within a number of iron (oxy-)hydroxide-sulfate minerals such as schwertmannite and jarosite. These minerals are soluble (releasing acidity as they hydrolyse) and could be an explanation for the dissolved iron measured in the aerated treatments on Days 7 and 21. In the dried/rewet slurries there was also an increase in dissolved Fe between Day 7 and Day 21, however this was less than in the continuously wet slurries because of the overall slower rate of oxidation, again possibly due to inhibition resulting from the aforementioned blocking by adsorbed organic complexes formed during the drying process.

What is interesting about Figures 4.3.6 and 4.3.7 is the relatively slow rate of sulfur oxidation (and concurrent slow release of Ca) in the aerated treatments during the first half of the experiment. The rate of pyrite oxidation by oxygen is reputably a slow process, while the rate of pyrite oxidation by Fe^{3+} is many orders of magnitude faster (Singer and Stumm, 1970). The curved shape of the lines in Figure 4.3.7 are consistent with first-order reaction kinetics for the production of sulfate ($S^{2-} + O_2 \rightarrow SO_4^{2-}$). The rate constants (*k*) determined graphically from the slopes of the plotted ln-transformed data are 0.027 and 0.026 mg L^{-1} day $^{-1}$ for the continuously wet and dried/rewet peat respectively. This suggests that, although drying slows the oxidation of sulfide, it does not appear to affect the rate constant markedly (the rate constant in this case is the

natural logarithm of the proportion increase in $[SO_4^{2-}]$ since Day 7). First-order kinetics means that the change in $[SO_4^{2-}]$ with time is a function of $[S^{2-}]$ at that particular time. The fact that the oxidation of sulfide in this study followed first-order kinetics suggests that this was microbially driven (i.e. biotic rather than abiotic; Hossner & Doolittle, 2003; Pugh, Hossner, & Dixon, 1984). The most likely reason for the acceleration of oxidation over time is the decline in pH. Iron- and sulfur-oxidsing microorganisms (especially *Thiobacillus ferrooxidans*) substantially increase FeS_2 oxidation, and researchers have found that this effect is more pronounced at pH values <4 (Arkesteyn, 1980; Pugh et al., 1984; Singer & Stumm, 1970). Extrapolation of the increase in $[SO_4^{2-}]$ over time using the integrated rate equation for first-order reactions:

$$\ln \frac{[SO_4^{2-}]_t}{[SO_4^{2-}]_0} = kt \qquad (4.5)$$

indicates that, had the incubations been allowed to run for another 14 days, $[SO_4^{2-}]$ in the continuously wet peat would have reached 567 mg L^{-1}, potentially leading to very low pH.

Aeration resulted in significantly less TFP in the slurries when compared to the anaerobic treatments. This is because at the pH values encountered in these slurries, aeration results in co-precipitation of phosphates with Fe^{3+} and Mn^{4+}, and at the lower pH range, with Al^{3+}. In addition, the lower pH values in the aerated slurries would have promoted $H_2PO_4^-/H_2PO_4^{2-}$ adsorption onto clay minerals and amorphous oxyhydroxides (Stumm and Morgan, 1996). What is perhaps a little surprising, given the fact that TFP includes at least some organic P, is the minimal impact of drying on phosphorus release under aerated conditions. If drying results in increased mineralization of P and P-release associated with the death of biota (as hypothesized in the previous section), then one might have expected higher concentrations of TFP in the dried/rewet than in the continuously wet slurries, even under aerated conditions. Yet by Day 49 there was nearly twice as much TFP (although this was statistically non-significant, one-way ANOVA, n=6, p=0.10) measured in the continuously wet than in the dried/rewet aerated slurries, even though the pH in the former was lower (mean [n=6] 4.7 vs. 5.4).

4.4.2 Floc

4.4.2.1 Effects of drying/rewetting under anaerobic conditions

Compared to the continuously wet anaerobic slurries, the dried/rewet floc slurries had lower pH, higher EC, higher Fe, Ca and TFP, with opposing trends over time (i.e. pH increased, while EC, Fe, Ca and TFP decreased over time). Sulfate

concentration was similarly low in both anaerobic treatments. The most marked impact of drying was an initial 360 times increase in TFP, and although this did decrease over time, by Day 49 TFP concentrations in the dried/rewet anaerobic slurries were still 262 times higher than in the continuously wet slurries. Because of the magnitude of this impact it is conceivable that this would have been a major determinant of the changes in the other measured variables, making it rather difficult to discern which process caused which.

In contrast to the peat, there was significantly more dissolved Fe in the anaerobic dried/rewet floc slurries than in the anaerobic continuously wet ones throughout the incubation period (although the maximum concentration measured in the dried/rewet slurries on Day 7, 3.15 mg L^{-1}, still only represented 0.53% of the total sediment Fe). An explanation for this may be found in the extraction data presented in Chapter 6. In contrast to the peat, more Fe in total could be chemically extracted from the dried than from the continuously wet floc samples. It must be mentioned here that water repellence tests also revealed severe water repellence in the dried floc (although this was somewhat lower than in the peat – see Chapter 3). The main contributors to the increased Fe extractability were an increase in the extractability of the organic fractions (pyro-P- and $KClO_3$-extractable). As has been suggested in Section 4.4.1.2 for the peat slurries, the increased availability of organic carbon and nutrients brought about by the drying, may have increased the efficiency of Fe reduction by Fe reducing bacteria. Furthermore, the lower pH in the dried/rewet slurries would have increased the dissolution of Fe (hydr-)oxides. This last point is supported by the significant negative correlations between pH and Fe both over time (r^2= 0.96, $p<0.05$) and on each of the sampling days (all at least $p<0.05$). Therefore the decrease in Fe in the dried/rewet slurries over the sampling period was probably directly related to increases in pH.

Drying resulted in a significant decrease in pH in the dried/rewet anaerobic treatments compared to the continuously wet anaerobic slurries. The most plausible reason for this is the drying-induced release and accumulation of CO_2. This was much greater than in the anaerobic peat slurries presumably because of the more easily decomposable nature of the floc organic matter, and also the higher P and N content of the floc (see Chapter 3). The increase in pH over time may have been due to the gradual depletion of microbial substrates. The increasingly reducing conditions (see Appendix 4.4) would also have produced alkalinity, as would other buffering mechanisms such as

carbonate and silica buffering. However, in non-calcareous soils*, the major buffering mechanism arises from specific ion adsorption at variable-charge sites, in particular those associated with the dissociation of humic acids, principally carboxylic acids (Bache, 1984):

$$R.COOH \underset{H^+}{\overset{OH^-}{\rightleftharpoons}} RCOO^- \qquad (4.6)$$

In this case then, the acidity produced by the increase in P_{CO_2} would have been at least partially buffered by exchange of calcium (calcium being the dominant cation; see Chapter 3) adsorbed on humic acids for H^+:

$$R.(COO)_2Ca \rightarrow R.(COO)_2^{2-} + Ca \text{ (desorption of calcium)} \qquad (4.7)$$

$$R.(COO)_2^{2-} + 2H^+ \rightarrow R.(COOH)_2 \text{ (adsorption of hydrogen)} \qquad (4.8).$$

This is consistent with the dry anaerobic slurries having the highest [Ca] of the floc treatments. The slowness of the recovery of pH over time may in part also have been contributed to by the lack of primary productivity since the slurries were kept in the dark.

If the accumulation of CO_2 was responsible for the decline in pH, this would indicate very intense microbial activity. Evidence for the intense microbial activity was provided by the overpowering odour emanating from the dried/rewet anaerobic slurries. The source of this odour deserves a brief discussion, since (1) drying markedly increased the odour from the anaerobic floc samples; (2) even the aerobic dried/rewet floc slurries emitted an odour, although less than the anaerobic ones; (3) odour from the anaerobic peat samples was very much less intense, and also different. It is generally assumed that the source of the foul odour from stagnant pools and swamps is due to H_2S, colloquially termed ‘swamp gas’ or ‘rotten egg’ gas. However, volatile organic sulfur compounds (VOSC), primarily as dimethyl sulfides (DMS), are also emitted in appreciable quantities from wetlands (Lomans et al., 1997), and are certainly also odorous (Ikawa, Sasner, & Haney, 2001; Watson, 2003). The malodours result mainly from the microbial degradation of S-containing amino acids and methoxylated aromatic compounds from senescing algae to DMS, and to a lesser extent, methanethiol (Lomans et al., 1997). Volatile organic sulfur compounds are generally associated with phytoplankton, especially bluegreen algae (Ikawa et al., 2001; Jenkins et al. in Ponnamperuma, 1972; Watson, 2003). It is therefore most probable that the bulk of the

* I am not aware of any published references in the aquatic literature.

organic matter in the floc samples are of algal, rather than macrophytic origin, while the peat sediments probably primarily originate from terrestrial vascular plants (see Chapter 3). It would appear then that drying shattered the organic material in the samples, causing the release of dissolved organic carbon upon rewetting (as mentioned previously). The sulfurous and aromatic compounds which now form part of the dissolved organic carbon pool are much more easily degraded due to their smaller molecular size, and especially in the presence of the high nutrient concentrations prevalent in the dried/rewet anaerobic slurries.

All of the reasons given in 4.4.1.2 for the higher concentrations of TFP in the dried/rewet, compared to the continuously wet anaerobic slurries also hold for the floc slurries. The impressive difference in magnitude is primarily due to the higher total P concentrations in the suspended sediment (Chapter 3). Interestingly though, in spite of the very much higher sediment P concentration in the floc, compared to the peat, less TFP was released in the continuously wet anaerobic floc than in the continuously wet anaerobic peat slurries. Nevertheless, drying appears to release proportionately much more P from the floc, than from the peat, suggesting that the floc organic matter is much more easily disrupted by drying. This theory is supported by the significantly higher $MgCl_2$-extractable P fraction in the floc than in the peat samples (~75% of total extractable P in the dried floc, compared to <5% in the peat; see Chapter 5). The decrease in TFP over time may be primarily due to bacterial uptake and the dissolution of the organic coatings formed upon drying, allowing the free ortho-phosphate proportion of the measured TFP to adsorb onto these 'freed' mineral surfaces (Guppy et al., 2005; Van Schreven, 1967).

4.4.2.2 Effects of aeration vs. effects of drying/rewetting under aerated conditions

Compared to the continuously wet anaerobic floc slurries, the continuously wet aerated slurries had more or less identical pH (around neutral) throughout the incubation period, slightly higher EC, similar [Fe] and [P], and slightly higher [Ca]. Only [SO_4^{2-}] was statistically significantly higher in the continuously wet aerated than in the anaerobic slurries (although this was less than half the concentrations encountered in the aerated peat slurries). This only slightly lowered the pH between Days 1-14, and then after an unexplainable rise between Days 14-21, again between Days 28 to 49. However, the pH remained around neutral throughout the incubation period, i.e. in the carbonate buffering range. This would normally lead to neutralisation of H_2SO_4 through precipitation of gypsum:

$$H_2SO_{4(aq)} + CaCO_{3(s)} + 2H_2O_{(L)} \rightarrow CaSO_4.2H_2O_{(s)} + H_2CO_{3(aq)} \quad (4.9)$$

Further reactions of the dissociation products of carbonic acid with water result in the production of OH^- ions, increasing pH. The effectiveness of this buffering effect will depend on the amount of acid released and the amount of $CaCO_3$ available for neutralisation. However the graphs in Figures 4.3.13 and 4.3.14 do not indicate gypsum formation. It is possible that the nature of the floc organic matter and the nature of the sulfides are such that, at least under aerated conditions, acidity is either prevented from forming or is effectively buffered. For example, the negatively charged persulfide on the pyrite surface attracts positive ions (e.g. Fe^{2+}) but this is not sufficient to fully compensate for the positive charge of such a cation (Parker & Robertson, 1999). Evangelou & Huang (1994) suggested that pyrite or surface-adsorbed Fe^{2+} reacts with CO_3^{2-} to form a pyrite/surface Fe(II)-CO_3 complex which counteracts this charge imbalance. If this were the case in the Lake Goollelal floc it may be possible that the adsorbed CO_3^{2-} would either slow or buffer the oxidation of sulfides. Another possible explanation for the minimal impact of aeration on pH is the very high concentration of TFP in the floc. Anions such as $H_2PO_4^{2-}$ can stimulate or inhibit oxidiation due to their complexation constant and also their ability to facilitate electron transfer (Evangelou & Huang, 1994). Harahuc, Lizama, & Suzuki (2000) found that sulfur oxidation in iron-grown *T. ferrooxidans* cells was stimulated at low phosphate concentrations but inhibited at high phosphate concentrations. Sulfur-grown cells, on the other hand, showed inhibition only at high phosphate concentrations. It would be interesting to pursue these relationships at Lake Goollelal with further research.

In the slurries from Sites 1-5, even though there was still a net SO_4^{2-} release, these mechanisms were still effective on Day 49, with only minimal pH decline. However, in the Site 6 slurry which had much higher total sediment sulfur (as well as 3.9% total chromium-reducible S, compared to 1.5% in the Site 3 sample) and lower total [Ca] than the other 5 sites, the pH decreased much more drastically over time (from 6.4 on Days 1 and 7 to 2.6 on Day 49). This coincided with gradually increasing $[SO_4^{2-}]$, so that on Day 49 the total $[SO_4^{2-}]$ was 1716 mg L^{-1} (compared to a mean of 168 mg L^{-1} for n=5). Likewise Ca concentrations in the Site 6 slurry increased from 28 mg L^{-1} on Day 7 to 173 mg L^{-1} on Day 49 (compared to a mean of 70 mg L^{-1} on Day 1 to 79 mg L-1 on Day 49 for n=5), or ~76% of total sediment Ca released on Day 49, compared to only ~17% for n=5. Since SO_4^{2-} was still increasing in the aerated continuously wet slurries (n=5) on Day 49, it is to be expected that, had the incubations

been allowed to run longer, and buffer capacity gradually becoming depleted, the pH would eventually have started to decline more rapidly, and a pattern similar to that observed in the peat slurries would have emerged.

As in the peat slurries, drying had the effect of 'dampening' the oxidative effects of aeration, with less SO_4^{2-} being released in the dried/rewet than in the continuously wet aerated slurries. However, instead of the pH gradually declining over time along with increasing [SO_4^{2-}] as in the peat slurries, this gradually increased from 6.2 on Day 1, to 8.1 on Day 49 suggesting that some other process was affecting pH. Apart from pH, the most obvious other difference in response to drying/rewetting under aerated conditions between the peat and the floc slurries was that in the floc slurries there was a massive release of TFP. This was less than that released by the dried/rewet anaerobic slurries, but nevertheless significantly more than that released by the continuously wet aerated slurries (see Figure 4.3.15). Qui & McComb (1994) also reported much higher P release from air-dried/rewetted intact sediment cores from North Lake than from ones kept continuously wet under aerated conditions. The fact that in the present study, the dried/rewet aerated peat slurries did not show an increase in P release suggests that Qui and McComb's (1994) sediment was probably more similar in nature to the floc sediment of this study, although their indicated LOI was much lower (23% compared to a mean of 73% for the floc sediment in this study). As for the peat samples, Fe extraction data showed no indication of a drying-induced increase in Fe crystallinity (Chapter 6), therefore this can be discounted as a reason for the increased P-release.

The most reasonable explanation for the high P release in spite of aeration is the low Fe:P ratio in the floc (see also Chapter 3 and 5). Jensen et al. (1992) found that the increase in total P concentration in Danish lakes from winter to summer was lowest in lakes with high Fe:P ratios. They suggested that provided the Fe:P ratio is >15 (by weight) it may be possible to control internal P-loading by keeping the sediment oxidised. Giordani et al. (1996) later also found that in spite of strong reducing conditions phosphate (and sulfide) release was weaker in iron-rich sediments. The Fe:P ratios of the peats in this study were very much higher than 15 (mean 75, n=6), however, in the floc it was 14 (mean n=6, and 13 if Site 6 is excluded). It would appear then, that there may not have been enough Fe available to bind the P, and hence P was released even under aerated conditions. pH (~7 and ~8, compared to 5.4 to 6.3 in the aerated dried/rewet peat slurries) may have been a contributing factor. Sorption capacities of Fe(III) oxides decrease markedly above pH 6.5, while hydroxy-apatite

($Ca_{10}(OH)_2(PO_4)_3$) starts to precipitate at pH >~8 (Stumm and Morgan, 1996). The organic coatings formed upon drying would have exacerbated this, leaving all the drying-induced P release with nowhere to go. In addition, agitation of the sediments brought about by aeration may have contributed to the release of phosphate (Fabre, 1988). As in the dried/rewet anaerobic treatment, the decrease in [TFP] over time was probably mainly due to the increased availability of sorption sites as the organic coatings dissolved (Van Schreven, 1967), as well as to bacterial uptake (particularly in view of the fact that TFP includes at least some dissolved organic P) and precipitation (towards the end of the incubation period) with Ca.

If drying results in the breakdown of organic matter with associated release of phosphates, it is to be expected that nitrogen, too, will be released (Qui & McComb, 1996; Soulides & Allison, 1961). Given the large amount of P released, there were probably also very large amounts of nitrogen released in the dried/rewet aerated slurries. When organic matter breaks down, organic nitrogen is released. This is then further decomposed by bacteria to ammonia, and then to ammonium, generating alkalinity in the process:

$$\underset{\text{(urea)}}{NH_2CONH_2} + H_2O \rightarrow 2NH_3 + CO_2 \qquad (4.10)$$

$$NH_3 + H_2O \rightarrow NH_4^+ + OH^- \qquad (4.11)$$

This process (ammonification) is so efficient at neutralising acidity that it is used to treat acid mine drainage (Parker and Robertson, 1999). It can reportedly very quickly raise the pH of acid waters to pH 9 or higher, and the OH^- ions produced remove metals from the water column. Ammonification occurs both aerobically and anaerobically (Mitsch & Gosselink, 2000), and this (along with the other possible reasons mentioned above) would therefore also have contributed to the rise in pH over time in the dried/rewet anaerobic treatments. Under aerated conditions, the ammonium produced in the second reaction above, would be converted to nitrite, and then nitrate, by nitrifying bacteria, a process that produces H^+ ions. The aerated dried/rewet slurries appeared to have a strong tendency towards anaerobia in spite of the constant supply of air. This was evidenced by the odour emanating from them as well as the ORP measurements (see Appendix 4.4). It is conceivable therefore, that ammonification, nitrification and denitrification all occurred simultaneously. The preceding discussion is of course speculative, as nitrogen species were not measured. Nevertheless, other effective pH buffering mechanisms such as buffering by organic anions (which can accept protons

and hence buffer the pH; Fillion et al., 1999) are unlikely to result in pH values as high as the ones measured in the dried aerated floc treatments.

4.5 Summary and Conclusions

The experimental set-up was of course not designed to test all of the scenarios and hypotheses discussed in Section 4.4, but to identify the overall effects of drying on the transformations of the important chemical constituents, pH, ORP, EC, Fe, Ca, SO_4^{2-} and PO_4^{3-} under anaerobic and aerated conditions, and from these, infer processes responsible for changes from known relationships between variables (including unmeasured ones). Due to the inherent limitations associated with this type of study, the results from this experiment should be considered 'exaggerated' to some degree. For example, dried sediment was finely ground, increasing surface area and reactivity of the particles. In reality, drying produced hard aggregates (in both sediment types), that may not have been as reactive as ground sediment. Nevertheless, grinding apparently still left the dried sediment water repellent (i.e. organically coated). In addition, organic sediments that had never dried, as well as deionised refill water, were used. Other sediment types, and the effect of repeated drying/wetting were not investigated. Also, slurries were kept in the dark, so that primary production would not mask the primary responses (such as P dynamics and pH). Nevertheless, the benefits of this approach have been demonstrated in that responses were much more easily identifiable, some of which could easily have been missed if, say, filtered lake water had been used as refill water. In most instances, all of the null-hypotheses outlined in section 4.2.3 could be rejected.

The notion that drying induces water repellence in aquatic sediments just like it does in terrestrial soils and sediments, and that this significantly influences subsequent biogeochemical behaviour upon re-inundation, is a novel one. The major difference between the two sediment types appears to lie in the nature of their constituents, i.e. the floc consisted of very labile (i.e. easily ruptured by drying), nutrient-enriched organic (presumably plankton-derived) matter, while the peat was more refractory. Furthermore, the floc appeared to be relatively 'inert' under continuously wet, and especially under continuously wet/anaerobic conditions.

In summary, a once-off drying and rewetting event has had little effect on the peaty lake sediments under anaerobic conditions, apart from a small, but statistically non-significant (although sustained), increase in TFP. Aeration had a much more significant impact than drying in that more SO_4^{2-} was released, resulting in considerable decreases in pH, which led to the dissolution of Ca minerals. The dissolved Ca and

other (not measured) released cations would in the field be susceptible to loss via stream or groundwater flow, thus potentially decreasing the wetland's buffer capacity in response to future drought episodes. In addition, dissolved organic matter released as a result of drying and rewetting would also potentially be lost, and this would further reduce the wetland's resistance to repeated drought events (particularly in view of the protective role that organic coatings formed upon drying have). Drying significantly slowed the subsequent oxidation of reduced sulfur (i.e. the release of SO_4^{2-} and related decrease in pH) upon rewetting under aerated conditions. A possible mechanism is that organic coatings formed upon drying blocked the contact of oxygen with these surfaces upon re-inundation, thus limiting oxidation under aerated conditions. Under anaerobic conditions, these organic coatings may not only promote the dissolution of Fe, thus potentially releasing P, but also prevent sorption of phosphates by out-competing P for sediment sorption sites (a double-whammy in terms of P release).

Underlying processes in the flocculated sediment were in essence the same as those in the peat, however, because of the magnitude of the impact of drying, these sometimes manifested themselves differently, particularly under aerated conditions. Drying very markedly increased the TFP concentration in the anaerobic slurries. pH in the dried/rewet anaerobic slurries were significantly lower than in the continuously wet anaerobic ones, and this was interpreted as being due to the accumulation of CO_2 brought about by increased microbial activity, which in turn was caused by the high nutrient concentrations and drying-induced higher availability of labile organic matter. This lower pH was, together with the very strong reducing conditions (also resulting from intense microbial activity), responsible for higher dissolved [Fe], which may also have released some P. Recovery of pH was slow, compared to recovery of pH in the dried/rewet peat slurries. Not an obvious feature of the peat slurries, drying also markedly increased malodours emanating from the floc slurries.

As in the peat slurries, aeration significantly increased SO_4^{2-} in solution in the floc slurries (although this was much less than in the peat slurries). Unlike the peat slurries, however, this caused only minimal declines in pH (which remained around neutral throughout the incubation period). However, because $[SO_4^{2-}]$ was still increasing on Day 49, it is anticipated that buffer capacity would eventually be outstripped, and the pH in the aerated floc slurries would also start to decline more rapidly. As in the peat slurries drying significantly reduced the amount of SO_4^{2-} released under aerated conditions. Even so, pH in the dried/rewet aerated slurries was lower on Day 1 than in

the continuously wet aerated ones (presumably due to increased CO_2 partial pressure, resulting from increased microbial activity). However, unlike the peat slurries where pH continued to decline over time, from Day 7 onwards the pH in the dried/rewet aerated floc slurries increased over time. The high pH (mean of 8.1 on Day 49) was interpreted as possibly being the result of ammonification, spurred on by drying-induced release of organic nitrogen.

In conclusion, this study has demonstrated the governing role that organic matter plays in drought response of lacustrine sediments, both in terms of potential acidification and eutrophication. Wetlands exist that will have both a suspended flocculated layer and underlying peat, such as Lake Goollelal, or there may only be peat, or only a suspended flocculated layer overlying a largely mineral sediment. In terms of relevance to the 'real world', if a lake such as Lake Goollelal were to dry, ultimate responses would depend on a number of factors (e.g. severity of drying, rate of drawdown, etc., see e.g. review by McComb and Qui, 1998) not investigated in this study. The most important would undoubtedly be the quality of the refill water. If it were $CaCO_3$ rich, the potential for acidification, in spite of iron sulfide-rich sediments, would be minimal in the short term, especially when one takes into account the protective role of the hydrophobic coatings, and the strong buffering potential of the floc layer. However, eutrophication, with all its associated problems (e.g. midge plagues, toxic algal blooms etc.), would be a major issue. Where only peat (particularly pyritic peat) is present, the data from this study suggest that acidification (especially after repeated drying events) is a likely outcome. Much more detailed research into the precise mechanisms involved in drying-induced changes in organic matter, development of water repellence, and how these affect biogeochemical cycling of important elements, is warranted.

CHAPTER 5
PHOSPHORUS PARTITIONING IN PEAT AND SUSPENDED ORGANIC SEDIMENTS OF LAKE GOOLLELAL, WESTERN AUSTRALIA: EFFECTS OF DESICCATION

Abstract

Aquatic organic sediments are a large sink for nutrients, especially phosphorus (P). Drying and reflooding of such sediments often, but not invariably, results in increased mobilisation of P and associated eutrophication problems. The objectives of this study were to identify the distribution of P fractions of the organic sediments of Lake Goollelal, a permanent, shallow wetland on the Swan Coastal Plain, Western Australia, and to determine the effects of drying on this. A sequential fractionation scheme was used to identify and compare P partitioning in wet and dried peat and suspended floc sediments. There were marked differences in the amounts and partitioning of P between the two sediment types, and also between dried and undried samples. In the peat, ~84% of total sediment P was organically bound. Drying decreased P_{MgCl_2}, P_{NaHCO_3} and P_{CDB} (the potentially mobilisable P fractions). This was interpreted as being due to increased P sorption capacity of the sediment. At the same time there was a substantial increase in P_{NaOH}. Along with analysis of dissolved humic colour (measured as $gilvin_{440}$) in the extracts, this was interpreted as being evidence for drying-induced increase in solubility of humic matter and associated P.

In the floc ~77% of total sediment P was organically bound. In contrast to the peat, drying substantially increased P_{MgCl_2}. When P was added to the sediments (after having removed adsorbed/loosely-bound P) in the elemental fractionation study described in Chapter 6, both the dried peat and floc retained considerably more P than the wet sediments, suggesting an increase in P adsorptive capacity for both sediment types. In the case of the floc the most likely reason for the increase in $P_{MgCl_2}$was the very high amount of drying-induced mineralised P compared to Fe (and Al) content of the floc. There were probably not enough of these (oxy)hydroxides to sorb the huge quantities of P derived from the organic P fractions. As in the peat, drying increased the solubility of humic matter but humic colour in the floc extracts was markedly less than

in the peat, a reflection of either a different organic matter source, and/or degree of decomposition of the two sediment types.

Comparison of the fractionation results with an incubation study of the same sediments revealed that an apparent drying-induced increase in sediment affinity for P does not necessarily equate to less P being released upon re-inundation. Furthermore, significantly less P was released from the continuously wet sediments than potentially mobilisable based on P fractionation. On the other hand, more P was released in the dried floc incubations than potentially mobilisable, suggesting possible release from the NaOH and/or ashing/HCl P pools (considered to be largely unreactive organic P).

The data from this investigation highlight the importance of sediment characteristics such as pH and Fe:P ratio in predicting how drying will affect P cycling in aquatic sediments. Where nutrient-rich suspended organic floc is present, a large drying-induced increase in loosely-bound and exchangeable P can be expected to result in serious eutrophication upon rewetting.

5.1 Introduction

Aquatic organic sediments develop from a variety of detrital matter such as plant and animal remains, sedimenting suspended matter, plankton, micro-organisms and faecal pellets. Most of this matter becomes buried before it can be completely degraded and the nutrients recycled. Because of this, and combined with the high affinity organic compounds have for nutrients (including those from anthropogenic sources; Golterman, 1984), organic sediments are a large sink for nutrients. Drying and reflooding of such sediments often results in an increase of phosphorus (P) concentration in the water column (Lucassen et al., 2005; Qui & McComb, 1994; Szilas et al., 1998; Twinch, 1987; Van Haesebroeck et al., 1997), although the opposite has also been reported (Haynes & Swift, 1985; Jacoby et al., 1982; Sommer & Horwitz, 2001). Drying-induced increases in not only P but also other nutrients is thought to originate mainly from the breakdown of organic matter and the death of microbial biomass, and the subsequent stimulation of microbial activity (Crozier et al., 1995; Fierer & Schimel, 2002; Mitchell & Baldwin, 1998; Qui & McComb, 1995; Soulides & Allison, 1961; Sparling & Ross, 1988; Sparling et al., 1985). Drying induced increase in iron crystallinity has also been implicated in changes in P binding capacity, and hence P availability (Baldwin, 1996a; Lijklema, 1980; McLaughlin et al., 1981). Although nitrogen, carbon and phosphorus are implicated in accelerated eutrophication, the release of P is of particular concern because it is usually the key nutrient limiting aquatic plant and algal growth (Sharpley et

al., 1995). Aquatic sediments rich in organic matter tend to exhibit high total P concentrations, however the correlation between sediment P and the concentration of P in the overlying water is at best modest to weak (Jensen et al., 1992; Wetzel, 2001). Therefore wetlands with organic sediments may be more severely affected by the release of P resulting from drying and rewetting, than less organic ones.

As drying, especially repeated drying/wetting cycles, can bring about irreversible changes in P cycling it was deemed important to investigate the effects of drying on sediments with no past history of drying. Lake Goollelal, a permanent water body on the Swan Coastal Plain (SCP), Western Australia, is an example of a wetland with high sediment P content, but comparatively low P concentration in the water column (1996-2004 mean winter concentration ~5 μg L^{-1}; mean summer concentration ~13 μg L^{-1}, see Appendix 3.8). Aquatic organic sediments tend to be heterogenous, and it was shown in Chapter 4 that whilst drying and rewetting of the peat sediment from Lake Goollelal resulted only in a statistically non-significant increase in P release under anaerobic conditions, drying and rewetting of the overlying suspended organic floc resulted in substantial release of P under both anaerobic and aerobic conditions. Suspended detrital floc is a feature in a number of SCP wetlands, both permanent and seasonal ones (some of which are currently being artificially supplemented with water in order to prevent them from drying; Horwitz & Benier, 2003). These flocs (variously coined sapropel, *Gyttja*, *Dy*, suspended organic detrital floc, flocculent organic matter etc., depending on context and composition – see Chapter 3) form from the exudates or degradation products of phytoplankton, bacteria and aquatic macrophytes via various physical, chemical and biological means (Leppard & Droppo, 2005). They consist of bacteria, viruses and other small organisms, aggregated humic substances, clay minerals, colloidal iron and manganese oxyhydroxides, biogenic silicates, bacterial envelope fragments, algal scales, cell lysis products, and both mineral and organic nanoscale coatings (Leppard and Droppo, 2005). As shown in Chapters 3 and 6, anaerobic flocs can also contain substantial amounts of iron sulfide. Flocs are very porous, rigid and highly hydrated (up to 80% water) which forces their density towards the density of water and prevents them from settling (Droppo, 2001).

As demonstrated in this study (see Chapters 3 and 4), and in the Everglades, Florida, 'suspended organic detrital floc', although much lower in bulk density than peat, typically had a much higher P content (Noe et al., 2003). Suspended organic flocs containing humic substances can have remarkable long-term stability with residence

times of centuries (Wilkinson & Reinhardt, 2005). Childers, Ross, & Leonard (2003) suggested that in the Everglades marsh drydown is the primary mechanism by which floc becomes part of the consolidated sediment component.

Whilst drying may not have an effect on the total size of the P pool, there may be a marked influence on its fractional distribution (Twinch, 1987), and consequently on its bioavailability upon reflooding. Phosphorus is usually divided into four or five general fractions (Ruttenberg, 1992; Wetzel, 2001): soluble phosphate P, exchangeable or loosely sorbed P, Fe-bound P, Al-bound P, Ca-bound P and residual organic P. Differentiating between the partitioning of these different fractions in the two sediment types should help to better understand their different behaviours, particularly in response to drying/rewetting. Unfortunately, a standardised fractionation scheme for P still doesn't exist, although this shortcoming has been acknowledged (Ruban et al., 1999). Sequential fractionation involves a series of successive chemical treatments of a sample, each being more drastic in action, or targeting a different phase, than the previous one. Numerous such schemes for phosphorus fractionation exist (e.g. Chang & Jackson, 1957; Hieltjes & Lijklema, 1980; Olsen & Sommers, 1982; Psenner & Puesko, 1988; Ruttenberg, 1992; Williams, Jacquet, & Thomas, 1976). Baldwin (1996b) used a modified version of the extraction scheme developed by Ruttenberg (1992, the 'SEDEX' extraction scheme) to characterise the phosphorus composition of aquatic sediments in eastern Australia, and in another study, to assess the effects of aeration and drying on phosphate sorption characteristics of a eutrophic reservoir (Baldwin, 1996a). As it was adapted to suit Australian organic sediments, this is the scheme that was adopted in this study (with some minor changes, see Figure 5.2.1).

The aim of this study was to identify and compare P partitioning in dried and undried aquatic peat and suspended organic floc from Lake Goollelal. The results from the investigation are used to explain observed differences in P release in incubations of the same sediments (Chapter 4).

5.2 Methods

5.2.1 Study site, sample collection and preparation

The study site, sample collection and preparation methodologies have been previously described (Chapter 3). A detailed characterisation of the Lake Goollelal sediments is also given in Chapter 3. The fractionation scheme described below requires

a large number of steps (including repeated extractions of individual phases) and replicates. In addition filterable reactive phosphorus (FRP) must be analysed immediately after extraction. Hence, due to limited time and resources not all of the sediment samples used in the incubation study (Chapter 4) could be fractionated. Peat and floc samples from two locations (known to have high sediment sulfur, iron and phosphorus concentration – see Chapters 3 and 4) were therefore selected from the eastern side of the lake (Sites 3 and 6 – see Figure 3.1.1b, Chapter 3), and analysed for two treatments – dried and wet (= two sites x two sediment types x two treatments x 3 replicates x 6 phases; plus multiple extractions and blanks).

5.2.2 Elemental fractionation and laboratory methods

The sequential P fractionation scheme used follows that described in Baldwin (1996b) with some minor modifications, and is shown schematically in Figure 5.2.1. The procedure used was as follows.

The wet samples were first centrifuged (under anoxic conditions) to remove porewater, then approximately exactly 2 g of this was weighed into 50-ml *Falcon* centrifuge tubes that had been preflushed with ultra high-purity N_2 gas. For the dried samples, 0.5 g of air-dried sediment was used (more of the wet sediment was used to take into account water content). Subsamples of the wet and air-dried sediment were oven-dried at 105°C in order to determine equivalent oven-dry weights. For the wet sediments, reagents were first de-gassed, and the first three steps in the scheme were carried out under anaerobic conditions. Forty-five ml of each extractant solution was added to the centrifuge tubes and these were then shaken for 16 hours at room temperature on an orbital shaker (*Ratek Instruments Australia*). The tubes were then centrifuged on a *JUAN* centrifuge at 3,400 rpm for 30 minutes. Supernatant solutions were extracted with a syringe and filtered (PALL Metrigard^{TM} GFC, 0.50 μm). Each extraction was carried out in triplicate and blanks were run throughout the procedure. As in Baldwin (1996b), extraction of each phase was repeated with fresh extractant solution until the level of filterable reactive phosphorus (FRP) in the supernatant was less than 100 μg L^{-1} (apart from the CDB leach, see below). This was done in order to ensure complete removal of individual phases and negated the need for $MgCl_2$ washes in between extractions (which was proposed by Ruttenberg (1992) in order to prevent problems associated with secondary adsorption onto residual solid surfaces).

After appropriate dilution, FRP was analysed by the ascorbic acid-combined reagent method (Eaton et al., 1995) and sample absorbances were measured on a

spectrophotometer (*Shimadzu* Model V1201). Where extracts were still coloured after dilution (as in the NaOH extracts), a blank of the sample was prepared to which only H_2SO_4 and NH_4-molybdate were added. Absorbance of this sample was deducted from the absorbance of the sample with the combined reagent. Prior to analysis, and where necessary, the $MgCl_2$ (phenolphthalein), $NaHCO_3$ (methyl red) and NaOH (phenolphthalein) supernatant solutions were neutralised with 10M H_2SO_4, and the HCl (methyl red) supernatant with 10M NaOH. Subsamples for total filterable phosphorus (TFP) determination in the $NaHCO_3$, NaOH and HCl extracts were stored frozen and then digested in an autoclave with NaOH-K_2SO_4 (Eaton et al., 1995), before appropriate dilution and analysis by the ascorbic acid-combined reagent method. Filterable non-reactive phosphorus (FNRP), which can be interpreted as consisting mainly (but not exclusively) of organic P, was calculated as the difference between TFP and FRP.

The citrate-dithionate-bicarbonate (CDB) reagent was prepared by mixing 0.30 M $Na_3C_6H_5O_7.2H_2O$ and 1.0M $NaHCO_3$ (pH 7.6), and dissolving 1.125 g of $Na_2S_2O_4$ into 45 ml of this solution. The CDB extracts were initially exposed to air in order to oxidise the dithionite, then acidified to pH <2 with HNO_3 (which had to be added very slowly and carefully in order to prevent development of cloudiness) before analysis for TFP by inductively coupled plasma spectrophotometry (ICP-AES) at the Marine and Freshwater Laboratory at Murdoch University. This was done because of interference of the citrate-dithionite buffer used in the extraction with the reduction of the molybdate-P complex. To nevertheless ensure complete removal of this phase, it was repeated with fresh extractant solution until $gilvin_{440}$ in the samples reached <10% of total $gilvin_{440}$.

Subsamples of each extracted phase (multiple extractions of individual phases were combined) were, where necessary, acidified to pH <2 with HNO_3 before ICP-AES analysis for total dissolved Fe, Mn, Al, Ca and S. The NaOH extracts were not acidified (because this would have caused the precipitation of humic acids), but kept in a cool room (4ºC) until ready for analysis. In addition, optical absorbances at 440 nm (coloured dissolved organic matter, or gilvin) of the $NaHCO_3$, CDB and NaOH extracts were measured on the *Shimadzu* spectrophotometer. This was done in order to estimate the dissolved organic carbon, DOC, concentration in the individual extracts. Absorption

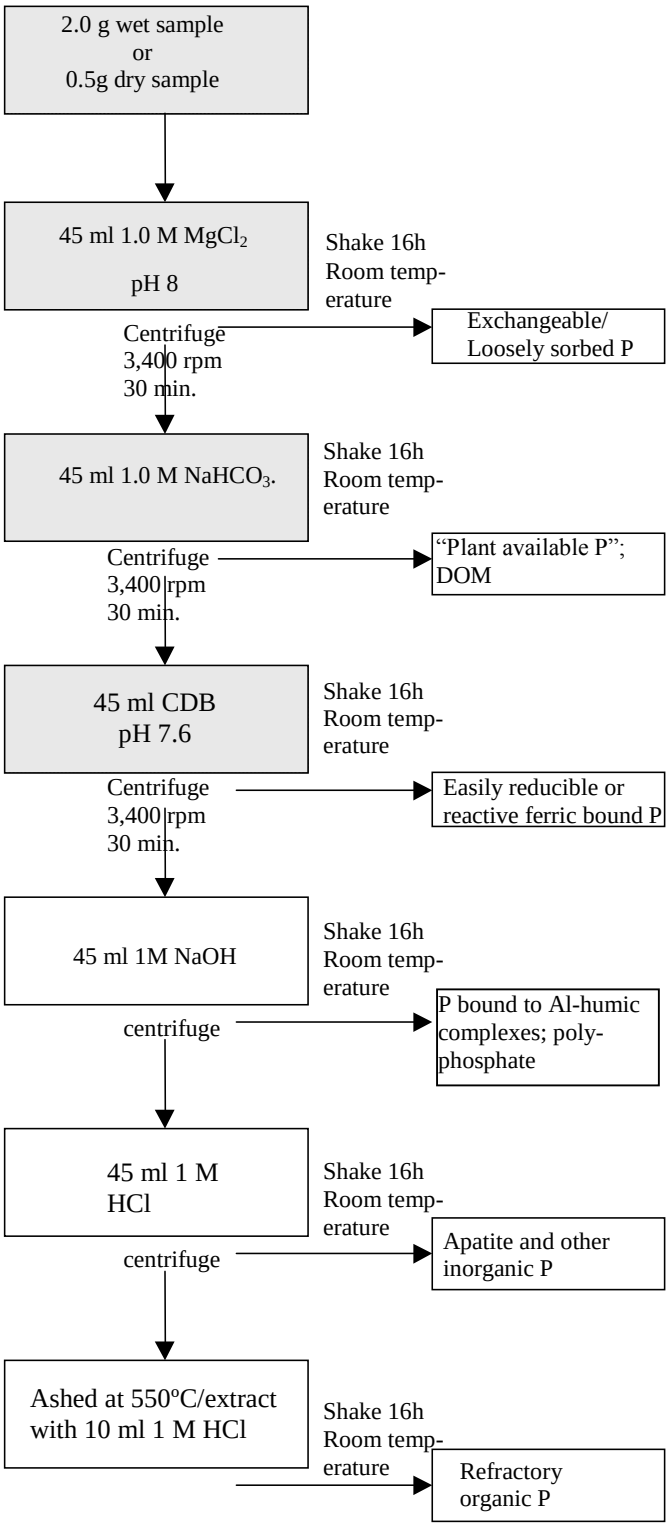


Figure 5.2.1: Schematic of the phosphorus sequential extraction procedure (Ruttenberg, 1992) as modified by Baldwin (1996b) with some adaptations. Shaded boxes indicate that extraction was carried out under anoxic conditions.

at 440 nm was found to be an excellent proxy for DOC concentration in river water (Yacobi, Alberts, Takacs, & McElvaine, 2003). Measurements were made in 1 cm quartz cuvettes, using the respective extractant solutions as blanks, and the $gilvin_{440}$ absorption coefficient was calculated as:

$$gilvin_{440}\ [m^{-1}] = 2.303\ A(440\ nm)/l$$

where l is the cuvette path length in metres. UV 254 measurements were also made on the $NaHCO_3$ extracts for comparison with the 440 nm readings. It was found that absorbances from the two wavelengths were well correlated (r^2= 0.93; n=21), and therefore measurements at 254 nm were dispensed with (since they were more complicated to make, requiring special quartz cuvettes and high degrees of dilution). In an attempt to characterise the humic matter in the extracts absorbances at 465 and 665 nm were also measured. The ratio of 465:665 (E_4:E_6) has long been used as an indicator of molecular weight and aromaticity of humic substances (i.e. the lower the ratio, the higher the aromaticity and molecular weight; Chen, Senesi, & Schnitzer, 1977).

5.2.3 Statistical analyses

General descriptive and explorative statistics were mainly used to describe the data. Simple correlations (Pearson's coefficients) were carried out in order to elucidate relationships between P fractions of wet and dried sediments and co-extracted elements (Fe, Mn, Al, Ca and S). Statistical analyses of differences between treatment and sediment types could not be performed because only two replicates were measured (the triplicate samples of each analysed being 'pseudo-replicates').

Correlation-based principal component analyses (Primer for Windows Package v. 5.2.1) were used to summarise patterns of (normalised) elemental distribution and treatment effects (i.e. dry/wet; peat/floc). This type of analysis is particularly useful for the ordination of environmental data. Its aim is to find a set of orthogonal vectors in the data space that accounts for as much of the data variance as possible. The data are projected from their original multi-dimensional space (representing the full set of environmental variables, or principal components) onto a reduced-dimensional subspace spanned by these vectors which should retain most of the intrinsic information in the data. The first principal component axis shows the direction in which the variance of sample points projected perpendicularly onto the axis is maximised. The second principal component is constrained to lie in the subspace perpendicular to the first.

Within that subspace, it points in the direction of the maximum variance. Then, the third principal component (if any) is taken in the maximum variance direction in the subspace perpendicular to the first two, and so on. In Primer, a correlation matrix is produced and this can be used to detect the strength of relationships between variables.

Two-way crossed ANOSIM (Analysis of Similarities, also in Primer) was used to detect significant differences between sediment types and treatment types. More details, including algorithms used, can be found in Clarke and Warwick (1994).

5.3 Results

5.3.1 Fractionation of P and co-extracted elements

Figure 5.3.1 shows the partitioning of the different fractions in mg P g^{-1} sediment for each site (n=3), while Figure 5.3.2 shows P partitioning in percentages of total sediment P (as the mean of Sites 3 and 6, which were calculated from Table 1 in Appendix 5.1). Means and standard errors are given in Appendix 5.1, Table 1. There were distinct differences in the amount of extractable P, and also in the partitioning of P fractions between the two sediment types. In total, for Sites 3 and 6 respectively, 0.365 and 0.332 mg P g^{-1} sediment was extracted from the wet, and 0.419 and 0.356 mg g^{-1} from the dried peat, compared to 1.895 and 1.781 mg g^{-1} from the wet floc and 2.589 and 2.720 mg g^{-1} from the dried floc (Figure 5.3.1). Compared to total sediment P as determined by XRF on sediment sub-samples, the scheme extracted 77.7% and 73.8% from the wet peat, 89.2% and 79.1% from the dried peat, and only 57.3% and 53.2% from the wet floc, and 78.2% and 81.2% from the dried floc (see Table 1 in Appendix 5.1).

P_{NaHCO_3} and P_{NaOH} (essentially the organic fractions) were the dominant P fractions (besides the non-extractable fraction) in the peat. In the wet peat these two reagents extracted similar amounts of P (Figure 5.3.1; Site 3 P_{NaHCO_3}: 0.122 mg g^{-1} or 33.5% of total extractable P, P_{NaOH} : 0.126 mg g^{-1} or 34.6%; Site 6: P_{NaHCO_3}: 0.103 mg g^{-1} or 31.2%, P_{NaOH}: 0.061 mg g^{-1} or 18.5%), and more of this tended to be in the non-reactive, than reactive form. Drying decreased P_{NaHCO_3} (from 33.5% and 31.2% to 16.5% and 19.5% of total extractable P for Site3 and Site 6 respectively) and markedly increased P_{NaOH} (from 34.6% and 18.5% to 56.9% and 55.9% of total extractable P). The great majority of this increase was non-reactive (FNRP; see Figure 5.3.1).

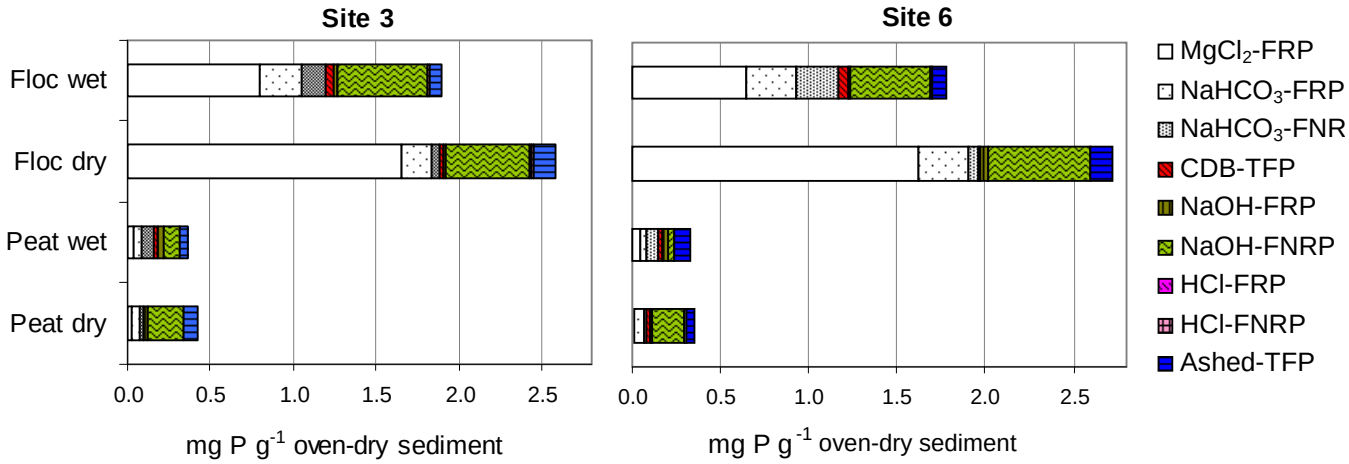


Figure 5.3.1: Distribution of P fractions in wet and dried peat and suspended floc from Lake Goollelal as determined by sequential extraction. FRP= Filterable Reactive Phosphorus; FNRP= Filterable Non-reactive Phosphorus; TFP= Total Filterable Phosphorus. (Standard errors are given in Appendix 5.1).

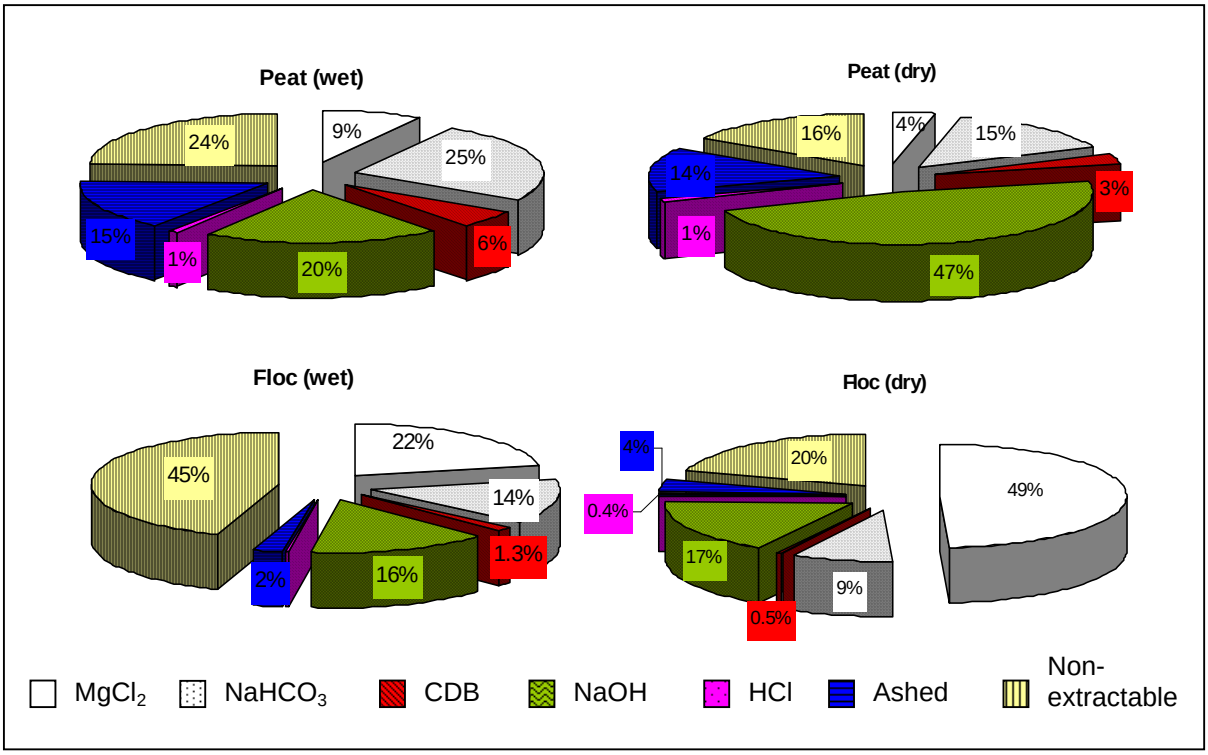


Figure 5.3.2: Distribution of P fractions in wet and dried peat and floc from Lake Goollelal as percentages of total sediment P (means of Sites 3 and 6).

In the wet floc, the extractable organic fraction (i.e., P_{NaHCO_3} + P_{NaOH}) was also the dominant P fraction (together comprising ~30% of total sediment P, mean of both sites, compared to ~45% in the wet peat), however there was a substantial non-extractable fraction of 45% of total sediment P (compared 24% in the wet peat). P_{MgCl_2} was also markedly greater in the wet floc (mean of 22% of total sediment P) than in the wet peat (mean of 9%, Figure 5.3.2). In the dried floc, P_{MgCl_2} increased from a mean of 22% of total sediment P to 49%. This is in contrast to the peat where drying decreased this fraction from a mean of 9% to 4%. On the other hand, drying decreased P_{NaHCO_3} in the floc from a mean of 14% to 9% of total sediment P, while there was no marked change in the NaOH fraction (Figure 5.3.2). In both sediment types drying improved total P extractability. In the peat non-extractable P was reduced from a mean of 24% to 16%, and in the floc from 45% to 20%.

High FNRP was associated with high gilvin values in the NaOH leaches of the wet treatments of both sediment types, even though, because of large differences in total sediment P content, the correlation coefficient when both sediment types were combined was negative (see Figure 1 in Appendix 5.3, and Appendix 5.2). Interestingly though, in the dried sediments, high FNRP was associated with low gilvin. This was because much less gilvin could be extracted from the dried Site 6 sediments, even though more FNRP could be extracted (see Figure 1, Appendix 5.3). NaOH which apparently extracts Al-bound P (Williams et al., 1976), co-extracted between 15.3% and 24.8% of total extractable Al (both sites, sediment types and treatment; see Table 4 in Appendix 5.1), and high TFP was associated with high Al concentrations in the leaches of the wet treatments of both sediment types (however, as mentioned above, when the sediment types were combined, there were no correlations between TFP and Al, see Appendix 5.3, Figure 2). As with gilvin, however, the relationships between NaOH-TFP and NaOH-Al in the individual sediment types was negative (see Appendix 5.3, Figure 2).

Figures 5.3.3 and 5.3.4 show the PCA ordinations for the $MgCl_2$ leach and the $NaHCO_3$ + NaOH leaches respectively. Co-extracted elements (Fe, Al, Ca, Mn, S [$MgCl_2$ and $NaHCO_3$ only], as well as gilvin [$NaHCO_3$ and NaOH]) were also included in the principal component analysis. Figure 5.3.3 ($MgCl_2$ leach) shows relatively good separation between treatment types (although there is an overlap with the Site 6 dry peat, which groups closest to the Site 6 wet peat); however the separation between

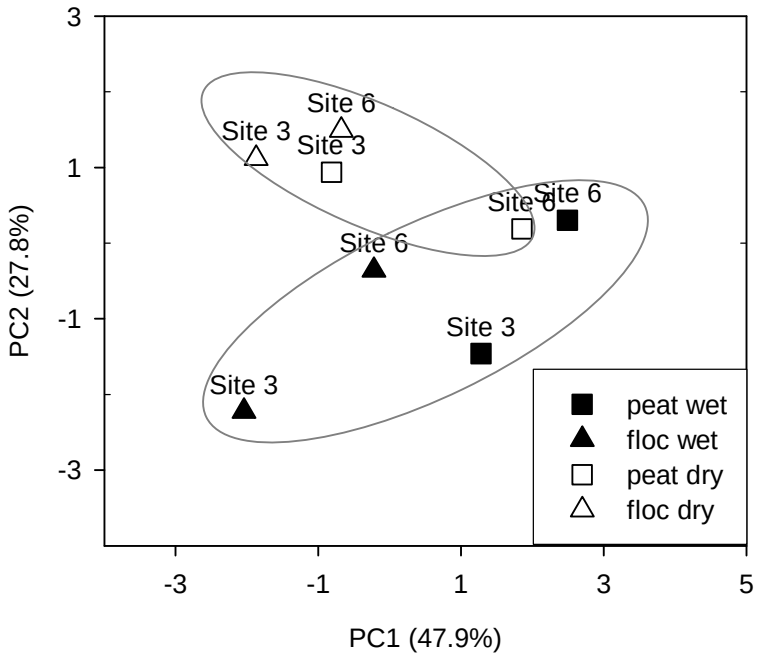


Figure 5.3.3: Two-dimensional PCA ordination of normalised concentrations of FRP and elements co-extracted with $MgCl_2$ from 'wet' and 'dried' sediments ('peat' and 'floc') from two sites from Lake Goollelal (Sites 3 and 6). PC1 and PC2 account for 75.7% of the total variability.

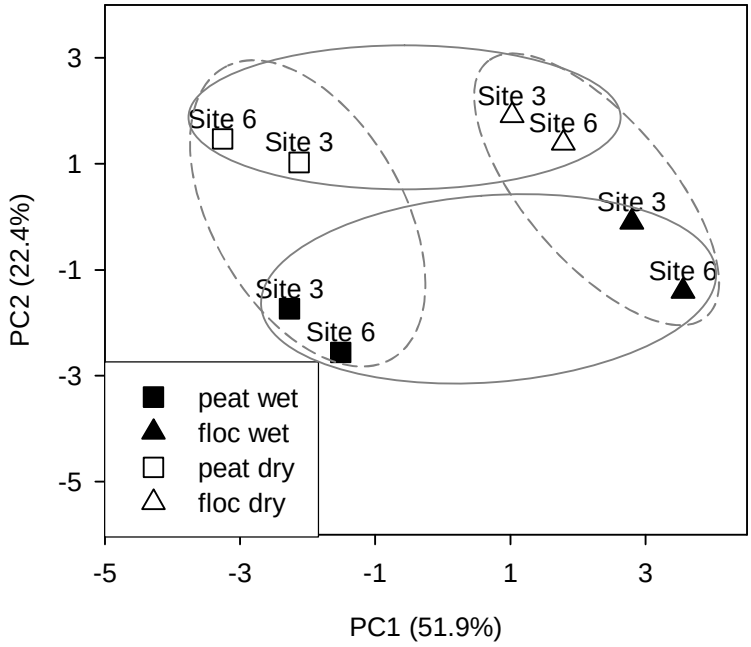


Figure 5.3.4: Two-dimensional PCA ordination of normalised FRP and FNRP concentrations (including gilvin and co-extracted Fe, S and Al) extracted with $NaHCO_3$ and NaOH from 'wet' and 'dried' sediments ('peat' and 'floc') from two sites from Lake Goollelal (Sites 3 and 6). PC1 and PC2 account for 74.3% of the total variability. The solid grey line points out treatment grouping, and the dashed grey line, sediment type grouping.

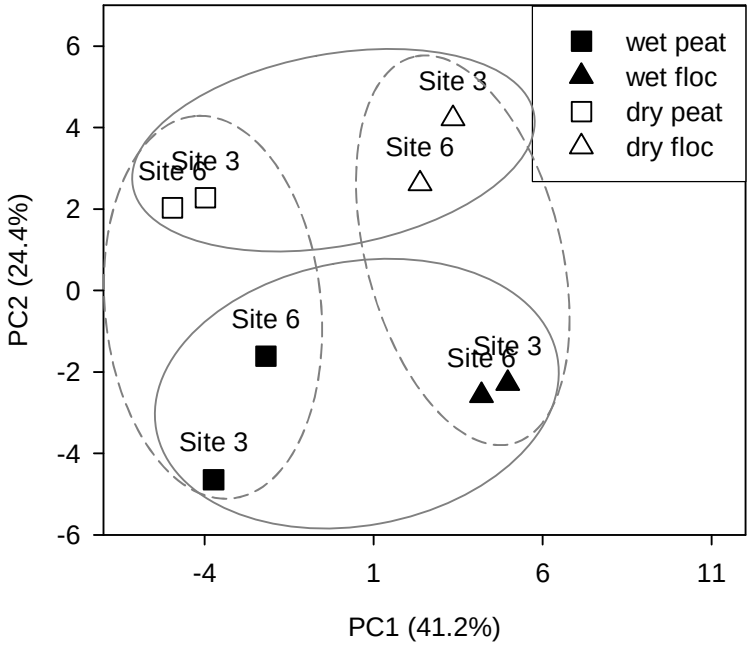


Figure 5.3.5: Two-dimensional PCA ordination of the extraction data using all five extractants and all co-extracted elements and gilvin (normalised data) from 'wet' and 'dried' sediments ('peat' and 'floc') from two sites from Lake Goollelal (Sites 3 and 6). PC1 and PC2 account for 65.6% of the total variability. The solid grey line points out treatment grouping, and the dashed grey line, sediment type grouping.

sediment types which is quite obvious from Figures 5.3.1 and 5.3.2 is not as pronounced. This is because the main drivers of the ordination were Fe and Ca (PC1 and PC2 explaining 75.7% of total variability between samples), and thus it reflects the differences in sediment concentrations of these elements (as well as FRP – see Appendix 5.2) between the two sites (rather than between sediment type; see Appendix 5.1, Tables 2 and 5). Magnesium chloride, as will be shown in Chapter 6 with NaOAc (sodium acetate, CH_3COONa), extracted substantially less Fe, but slightly more Ca, from all of the dried than from the wet samples. NaOAc-TFP, which was determined as part of the elemental fractionation scheme (Hall, Vaive, Beer, & Hoashi, 1996) described in Chapter 6, is presented in Table 1b in Appendix 5.1 for comparison. This fraction has been described as 'authigenic apatite' (formed in-situ) and $CaCO_3$-bound P by Ruttenberg (1992), and in the SEDEX scheme this is extracted after $MgCl_2$ and CDB extraction (i.e. after removal of loosely bound/exchangeable P and Fe-bound P). Table 1b in Appendix 5.1 shows that whilst NaOAc extracted comparable amounts of P from the dried floc sediments as the $MgCl_2$ extractant, it extracted ~50% more P from the wet floc, and up to 85% more P from the peat than did $MgCl_2$. Moreover, while $MgCl_2$

extracted less P from the dried than from the wet peat, more (33.33%) was extracted from the dried than from the wet peat by NaOAc.

In the principal component analysis of the $NaHCO_3$ + NaOH fractions there was very good separation of both treatment and sediment types (Figure 5.3.4). The ordination was influenced to a more or less equivalent degree mainly by $NaHCO_3$-FRP, $NaHCO_3$ and NaOH-extractable gilvin, and NaOH-FNRP (see Appendix 5.2). The first and second principal components explained 74.3% of total variability in the data.

The CDB reagent leached only 6% of total sediment P (based on a mean of both sites) from the wet peat, and drying decreased this amount to 3% (Figure 5.3.2). Even less was leached by this extractant from the floc, namely 1.3% of total extractable P from the wet, and 0.5% from the dried floc. There was no evident association between CDB-TFP and CDB-Fe in the wet samples of either sediment type, or in the dry floc samples. However in the dried peat samples high Fe was associated with high TFP (see Figure 3, Appendix 5.3). HCl extracted very negligible amounts of P from both sediment types and treatments, and most of this was non-reactive. This extractant, which is supposed to leach 'detrital apatite' and 'other inorganic P' (Ruttenberg, 1992) also extracted very negligible amounts of calcium from both sediment types (see Table 5, Appendix 5.1). There was however a relatively large component of 'refractory/organic' P, as determined by ashing followed by extraction with 1M HCl. In the wet peat 15% (mean of both sites) of total sediment P was extracted, and drying slightly decreased this to 14%. The proportion of P extracted from the floc by this means was smaller, namely 2% from the wet and 4% from the dried floc. Of the co-extracted elements only Al had a substantial proportion in this fraction, and total extractable Al itself represented only about half the total sediment Al as determined by XRF analysis (Table 4, Appendix 5.1). Although Fe in this refractory fraction was comparatively low (between 0.6% and 8.9% of total extractable Fe), total extractable Fe represented only between 16.8% and 47.07% of total sediment Fe as determined by XRF, suggesting that the scheme is not able to extract Fe associated with sulfides (see Chapter 6).

When all of the data were analysed together, the resulting PCA ordination (Figure 5.3.5) was very similar to that presented in Figure 5.3.4, highlighting the dominating role of the organic fractions in these sediments (the main drivers were more or less the same ones as in Figure 5.3.4). In spite of the obvious differences between both sediment types and treatment types, a 2-way crossed ANOSIM (which was carried

out in Primer after agglomeration of the standardised data using Euclidean distance) failed to produce significant differences between sediment types or treatment types. This was mainly due to the low number of replicates (i.e., two).

5.2.3 Efficiency of individual sequential extractions

Figure 5.3.6 shows the efficiency of individual $MgCl_2$ extractions of the different sediment samples. Samples with higher FRP concentrations required more extractions in order to remove an 'acceptable' proportion (i.e. to an arbitrary concentration of 100 μg L^{-1}) of FRP. The wet peat samples required only 1 extraction each in order to reach an extract concentration of < 100 μg L^{-1}, the dried peat of Site 6 also only required one, while the dried peat of Site 3 required two. FRP in the floc, however, was mainly $MgCl_2$-extractable, and hence it required five repeated extractions in order to reach this level in the wet floc. In the dried floc there was still ~ 200 μg L^{-1} of FRP in the extracts. However, the first two extractions of the dried floc already removed ~93% of the total amount extracted, while it took four repeated extractions of the wet floc to remove a similar level. The fifth extractions removed only an additional 3% from the wet, and 1% from the dried floc.

The efficiency of the $NaHCO_3$ extractions was similar to the first reagent in the sequence (Figure 5.3.7). The wet peat samples required two, the dried peat and the wet floc 3, and the dried floc four extractions to reach acceptable FRP levels. Again, although the third extracts of the dried floc still contained > 100 μg L^{-1} FRP, this represented ~93% of total FRP removed, a percentage higher than that of the third extracts of the other samples (Figure 5.3.7). Figure 5.3.8 demonstrates the lack of correlation between FRP and $gilvin_{440}$ in the individual extracts. Whilst the dried floc contained the highest concentrations of FRP, the dried peat samples contained the highest gilvin content, and gilvin content in the third dried peat extracts were higher than in the first dried floc extracts.

Because TFP content of the CDB extracts was analysed by ICP-AES (i.e. composite of all repeated extractions), $gilvin_{440}$ was used as an indication of the effectiveness of P removal of individual extractions (Figure 5.3.9). Similar amounts of gilvin were extracted with CDB from the wet samples (peat and floc) as with $NaHCO_3$, while ~1.4 – 2.4 times more was extracted with $NaHCO_3$ than with CDB from the dried samples (Table 7, Appendix 5.1). Figure 5.3.10 (a & b) shows that whilst two extractions were sufficient to reduce NaOH-FRP concentration in the extracts to an acceptable level, the second extracts, particularly of the dried peat, still contained

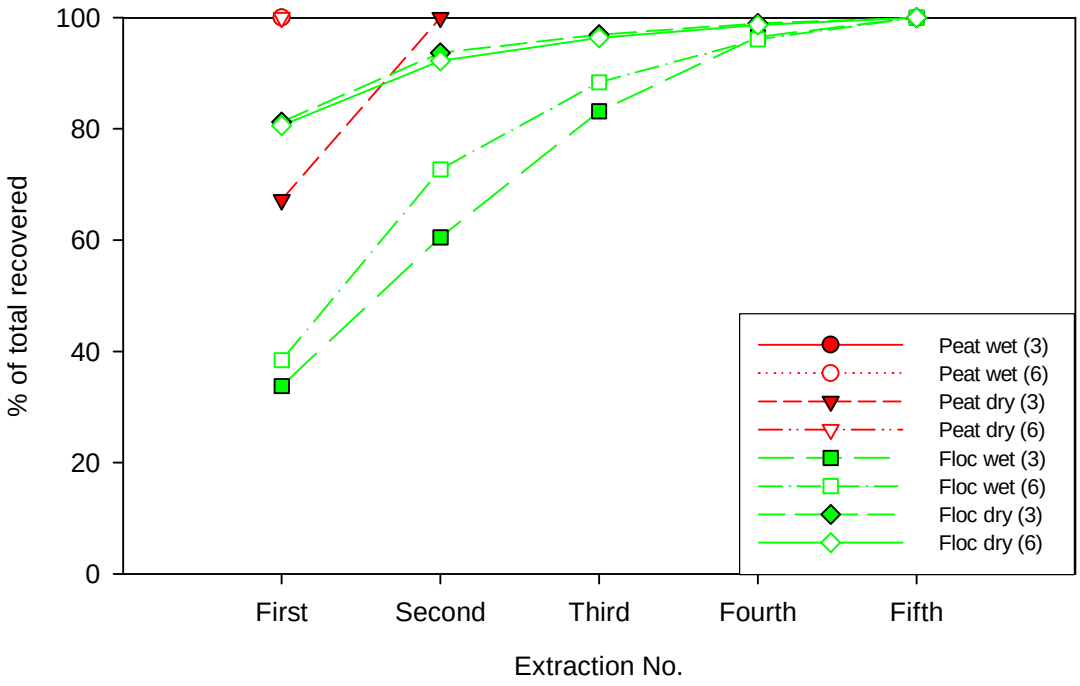


Figure 5.3.6: Percentage of total FRP recovered in individual $MgCl_2$ extracts of Lake Goollelal sediments.

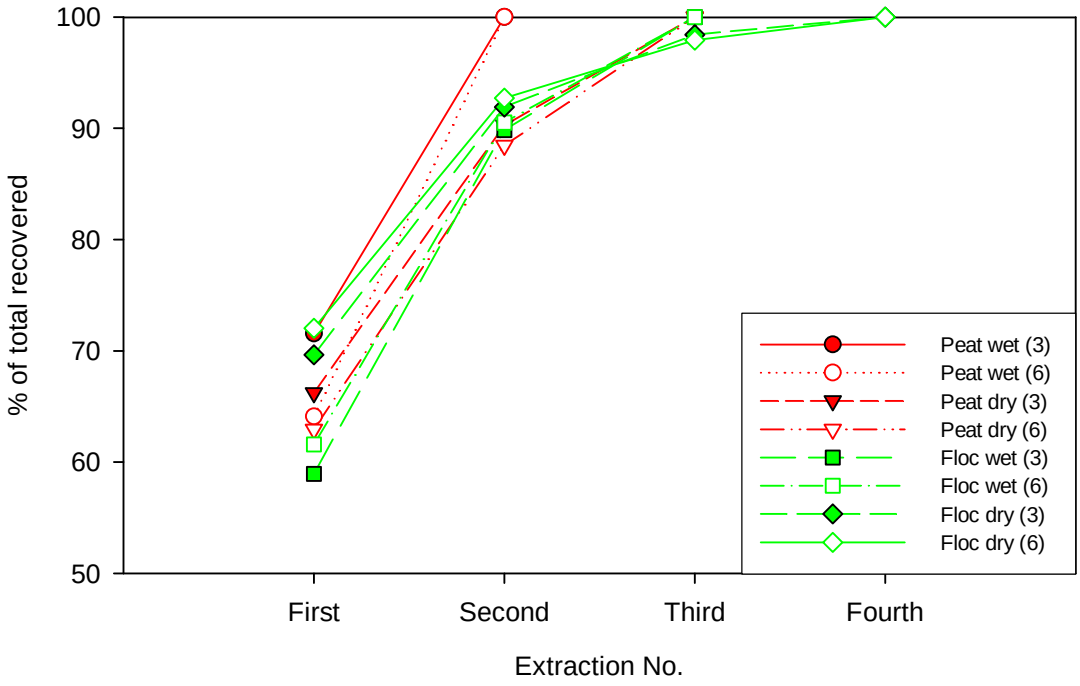


Figure 5.3.7 Percentage of total FRP recovered in individual $NaHCO_3$ extracts of Lake Goollelal sediments.

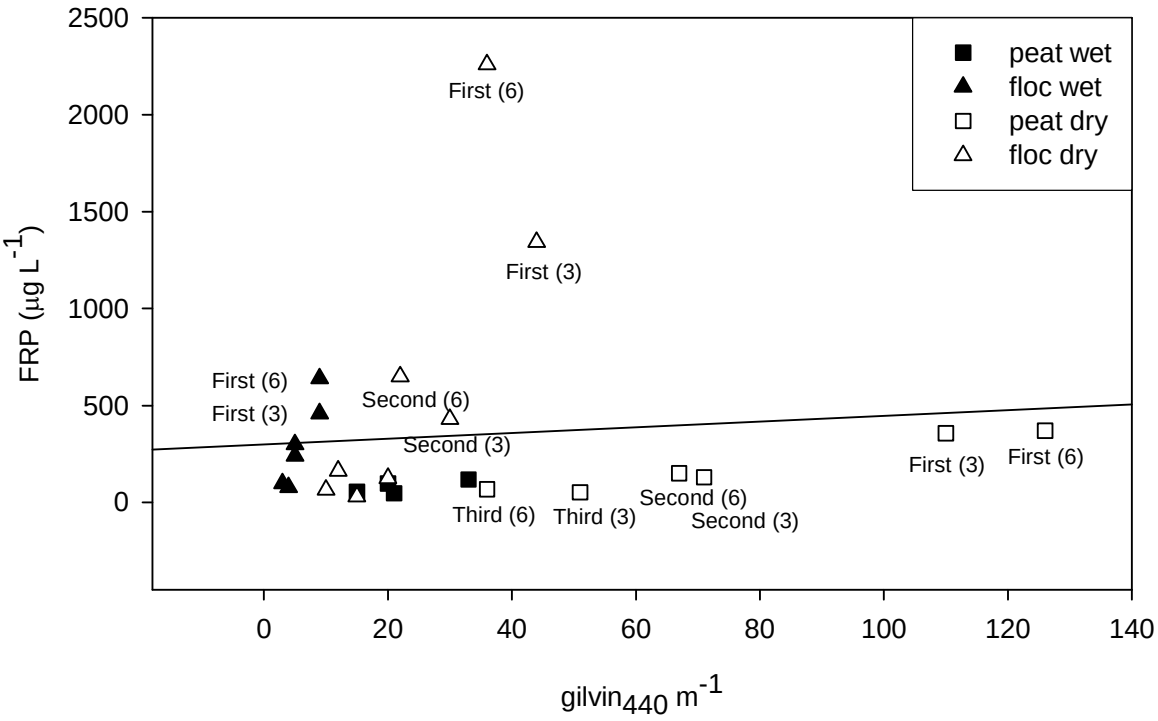


Figure 5.3.8: $Gilvin_{440}$ (colour) versus FRP in individual $NaHCO_3$ extracts of Lake Goollelal sediments. Labels are Extraction No. (Site). (Not all symbols are labelled due to over-crowding).

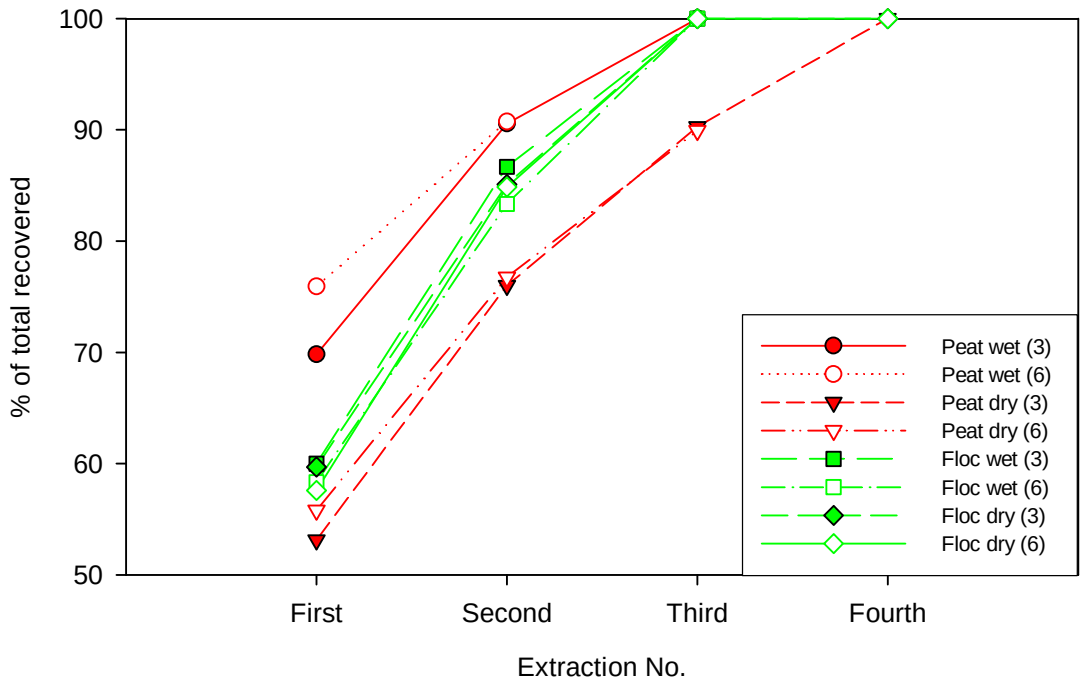


Figure 5.3.9: Percentage of total $gilvin_{440}$ recovered in individual CDB extracts of Lake Goollelal sediments.

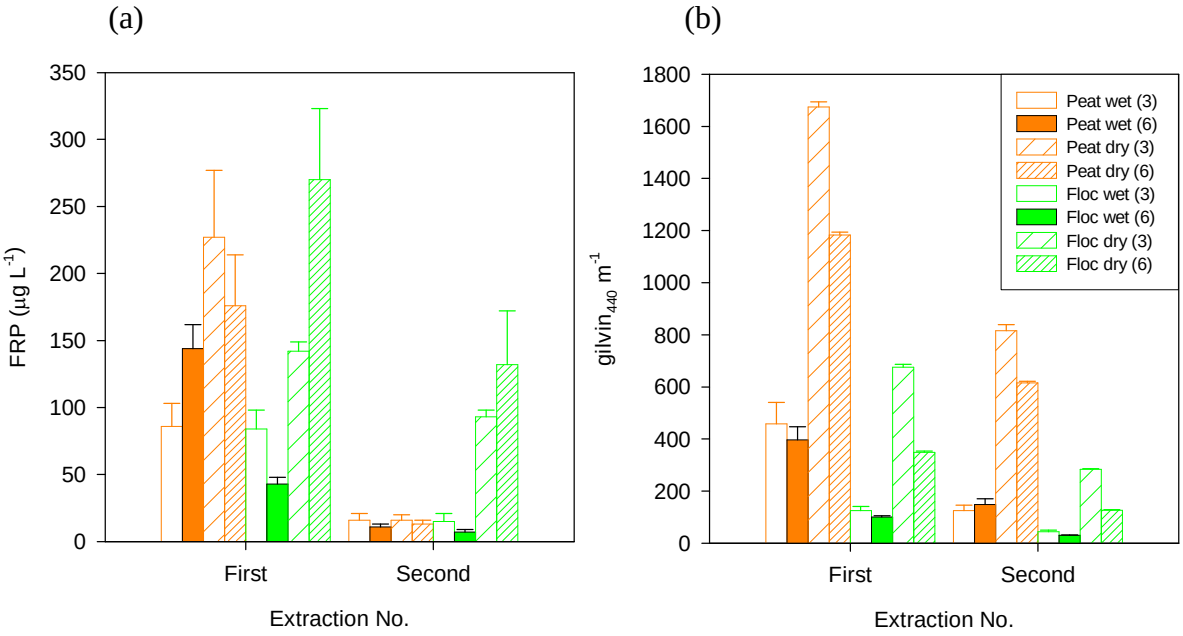


Figure 5.3.10: Concentration of FRP (a) and gilvin$_{440}$ content (b) in individual NaOH extracts of Lake Goollelal sediments. Error bars are standard errors (n=3).

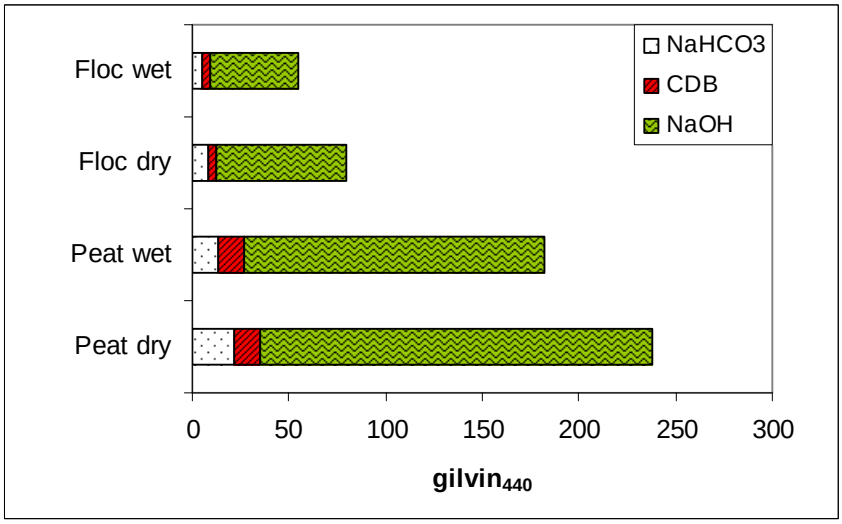


Figure 5.3.11: Distribution of humic colour (gilvin$_{440}$) fractions in wet and dried peat and floc from Lake Goollelal as determined by $NaHCO_3$, CDB and NaOH sequential extraction. Gilvin$_{440}$ is expressed as gilvin g^{-1} sediment L^{-1}. (Mean of 6 replicates from two sites; standard errors are given in Table 7, Appendix 5.1).

considerable amounts of gilvin. FRP in the NaOH extracts was not correlated with gilvin (however, as mentioned in 5.3.1, high gilvin was associated with high FNRP in these extracts, see Figure 1 in Appendix 5.3).

5.3.2 Dissolved humic colour (gilvin$_{440}$) in the $NaHCO_3$, CDB and NaOH leaches

Table 7a in Appendix 5.1 shows gilvin$_{440}$ extracted by the three reagents $NaHCO_3$, CDB and NaOH. Figures are expressed as gilvin g^{-1} sediment L^{-1}, and were calculated as follows:

$$\text{gilvin } g^{-1} \text{ sediment } L^{-1} = \frac{\left(\frac{\text{gilvin in the 45 ml extract} * 45}{1000} \right)}{\text{equivalent oven-dry weight of sample (g)}}$$

This conversion was done in order to standardise gilvin which allows comparisons between samples to be made. By far the highest amount of humic colour was extracted by NaOH, and on average ~1.5 times more was extracted from Site 3 than from Site 6. Figure 5.3.11 shows the same data as means of both sites. It can be seen that in all of the samples drying resulted in more $NaHCO_3$- and NaOH-extractable gilvin, but slightly less CDB-extractable gilvin. However drying did not affect the proportion of NaOH-extractable gilvin in the samples (Table 7c, Appendix 5.1). Both wet and dried samples of both sediment types contained ~85% of total extractable gilvin, while the proportion of $NaHCO_3$-extractable gilvin on average increased by a similar amount as CDB-extractable decreased (~1-2%).

E_4:E_6 ratios (ratio of absorbance at 465:665 nm) of the $NaHCO_3$ and NaOH extracts are presented in Table 5.3.1. The ratios (overall) were relatively low (between 3.9 to 6.7 in the peat, and between 4.2 and 6.4 in the floc). Drying increased the ratio in the peat (from a mean of 3.9 to 5.5 in the $NaHCO_3$ extracts, and from a mean of 5.3 to 6.6 in the NaOH extracts). In the floc, the ratio in the $NaHCO_3$ extracts decreased (from a mean of 6.45 to 5.0), while it increased slightly in the NaOH extracts (from 4.2 to 4.7). The ratios measured in the CDB extracts of the dried peat samples (these are the only ones that were made), i.e. a mean of 7.7, were the highest out of all of the extracts.

Table 5.3.1:

E_4:E_6 ratios of individual $NaHCO_3$ and NaOH extracts of wet and dried Goollelal sediments (standard errors are given in brackets, n=3).

Extractant	$NaHCO_3$					CDB	NaOH		
Extraction No.	First	Second	third	fourth	Mean	fourth	First	Second	Mean
Site 3 Peat wet	5.2 (.2)	3.0 (.9)			4.1		4.5 (.7)	5.8 (.1)	5.2
Site 6 Peat wet	3.0 (.2)	4.4 (.5)			3.7		4.7 (.9)	6.1 (.5)	5.4
Mean peat wet	4.1	3.7			**3.9**				**5.3**
Site 3 Peat dry	5.1 (.3)	5.1 (.3)	5.1 (.4)		5.1	8.7 (.4)	6.2 (.1)	6.8 (.0)	6.5
Site 6 Peat dry	6.1 (.0)	5.7 (.0)	5.7 (.3)		5.8	6.7 (.1)	6.4 (.0)	7.2 (.1)	6.8
Mean peat dry	5.6	5.4	5.4		**5.5**	**7.7**	6.3	7.0	**6.7**
Site 3 Floc wet	4.5 (.2)	6.3 (.8)	7.4 (2.1)		6.1		3.0 (.5)	5.0 (.1	4.0
Site 6 Floc wet	4.0 (.1)	10.8(1.7)	5.7 (1.7)		6.8		4.4 (.1)	4.3 (.2)	4.4
Mean floc wet	4.3	8.6	6.6		**6.4**		3.7	4.7	**4.2**
Site 3 Floc dry	3.1 (.6)	5.2 (.1)	5.2 (.2)	5.3 (.2)	4.7		5.0 (.0)	5.0 (.0)	5.0
Site 6 Floc dry	5.2 (.2)	5.3 (.3)	6.0 (.3	4.7 (.9)	5.3		4.4 (.1)	4.3 (.2)	4.4
Mean floc dry	4.2	5.3	5.6	5.0	**5.0**		4.7	4.7	**4.7**

5.4 Discussion

5.4.1 $MgCl_2$ extracts

One of the major differences between the two sediment types was the amount and proportion of P_{MgCl_2}. This phase is operationally defined as 'exchangeable/loosely sorbed' P and hence is the phase that is potentially most readily available to the biota (Baldwin, 1996b). Therefore changes in the size of this phase will greatly influence primary productivity. The drying-induced reduction of 'exchangeable/loosely sorbed' P pool in the peat sediments of both sites suggests an increase in adsorptive capacity of these sediments. This is consistent with the findings of Barrow & Shaw (1980), Jacoby et al. (1982), and Haynes & Swift (1985) who found that air-drying of field-moist soils increased the capacity of the soils to adsorb phosphate (and is obviously inconsistent with Twinch (1987), Qui & McComb (1994), and Baldwin's studies (1996a), where the opposite was found). It is also consistent with some of the experimental data from Chapter 6. When pyro-phosphate (as $Na_4P_2O_7.10H_2O$) was added to sediment samples from the same sites (after the removal of adsorbed/loosely-bound P with sodium acetate) in order to extract organically bound metals, the dried samples (both peat and floc) were much more efficient at retaining the added P (see Table 8, Appendix 5.1). The fact that drying increased P adsorption capacity suggests (and is again consistent with findings in Chapter 6) that there was no drying-induced increase in crystallinity of Fe and Al (oxy-hydroxides). An increase in crystallinity of these oxides would have

reduced their capacity to bind P because of decreased surface area (McLaughlin et al., 1981). The main reasons for the increase in P affinity are probably because drying resulted in a decrease in pH (see Chapter 4; Olila & Reddy, 1995), and also exposed additional mineral surfaces. Given the pyritic nature of the sediments, a further plausible explanation for the increased P affinity could be that oxidation prior to complete drying resulted in the transformation of ferrous sulfides to amorphous ferric (oxy)hydroxides (De Groot & Fabre, 1993). These have a very high affinity for P due to their large surface area.

It is interesting to note that the decrease in $MgCl_2$-P in the Site 6 dried peat (~10.8%) was much greater than in the Site 3 dried peat (~3.5%). This disparity most likely came about because of differences in sediment characteristics between the two sites. Although both sites had very similar chromium-reducible S (~1.45%), Site 6 had lower pH (6.2 vs. 6.9) and Ca (0.76% vs. 1.96%), and much higher Fe (5.58% vs. 2.78%) concentrations than Site 3 (see Chapter 3). Both Ca concentration and pH influence the amount of phosphate that can adsorb onto Fe(OOH) (Golterman, 1998). In non-calcareous soils and sediments (such as these) the P-binding capacity increases with decreasing pH because of protonation of surface Fe and Al functional groups in clays and in oxides and hydroxides of Al and Fe (Olila & Reddy, 1995). In calcareous sediments, the opposite is true; P sorption increases with increasing pH due to co-precipitation with $CaCO_3$ (Otsuki & Wetzel, 1972). The Fe:P ratio also appears to influence the P sorption capacity of sediments. Jensen et al. (1992) found that the increase in total P concentration in Danish lakes from winter to summer was lowest in lakes with high Fe:P ratios. They suggested that provided the Fe:P ratio is >15 (by weight) it may be possible to control internal P-loading by keeping the sediment oxidised. By analogy then, if the ratio is lower than this, there will not be enough Fe to bind the P, and P will be released even under oxic conditions. The Fe:P ratios of the peats in this study were very much higher than 15 (Site 3: 59, Site 6: 130, see Chapter 3), although most of the Fe was present as sulfides rather than (oxy)hydroxides. Giordani, Bartoli, Cattadori, & Viaroli (1996) later also found that in spite of strong reducing conditions phosphate (and sulfide) release was weaker in iron-rich sediments. These four factors then (pH, Ca and Fe concentrations, and the Fe:P ratio) would explain the differences in the amount of P_{MgCl_2} between the two sites. In addition to the aging effect of repeated drying/wetting cycles on Fe (oxy)hydroxides (Baldwin 1996a), these four factors may well also be the reasons for the contradictory reports in the literature (see above) regarding the effect of drying on P sorption capacity.

It is difficult to explain the different response (i.e. significant increase) of the floc sediment to drying in terms of $MgCl_2$-extractable P with the first three factors. pH of the peat and floc were virtually the same in the individual sites, sediment Fe and Cr-reducible S content was higher in the floc, and Ca content was similar. The Fe:P ratios though were markedly lower in the floc than in the peat. In the Site 3 floc this was 9, and in the Site 6 floc 19. This lower ratio is due to the very high P concentration (7 times higher than in the peat), and means that even though drying may have increased the adsorptive capacity of the Fe- and Al-oxyhydroxides (as evidenced by the afore-mentioned Chapter 6 pyro-P data, and the drying induced reduction in P_{NaHCO_3} and P_{CDB}) there were simply not enough of these to bind the enormous amount of P released as a result of drying. Furthermore, drying also released huge amounts of humic acids (see below), and there would have been competition between these and P for sorption sites (Guppy et al., 2005). The question arises as to where this P came from. If drying-induced increase in P release is mainly due to the breakdown of organic matter and the death of microbial biomass (Crozier et al., 1995; Fierer & Schimel, 2002; Mitchell & Baldwin, 1998; Qui & McComb, 1995; Soulides & Allison, 1961; Sparling et al., 1985; Sparling & Ross, 1988), then one would expect a shift in P away from the $NaHCO_3$ and NaOH pools to one or more of the other P pools. The data suggest that at least some of the drying-induced increase in $MgCl_2$-extractractable P in the floc may have come from the $NaHCO_3$-extractable pool, i.e. the more easily extractable organic pool. Results from the NaOH pool are conflicting however, Site 3 experiencing a slight decrease in P_{NaOH}, while in Site 6 there was an increase (more on the P_{NaOH} pool below).

The differences observed between amounts of P extracted with $MgCl_2$ and NaOAc (sodium acetate) warrants a brief discussion. One of the reasons why NaOAc extracted more P from the peat (both wet and dried), and also from the wet floc than did $MgCl_2$ could be that this reagent extracted some Al-bound P, as well as biogenic apatite (Ruttenberg, 1992). It is worth noting that both reagents extracted similar amounts of Ca when used first in the schemes (see Table 5 Appendix 5.1, and Table 4 Appendix 6.1). Ruttenberg's (1992) definition then of the NaOAc phase, which is extracted after $MgCl_2$, $NaHCO_3$ and CDB, as including '$CaCO_3$-bound P' (in addition to authigenic and biogenic apatite), is somewhat questionable (particularly in view of the fact that $MgCl_2$ washes were used in between extractions in order to prevent readsorption problems). Rapin, Tessier, Cambell, & Carignan (1986) likewise used a scheme in which NaOAc is used after $MgCl_2$ to extract 'metals bound to carbonates or specifically adsorbed'. In the present study $MgCl_2$ extracted ~90% (Site 3) and ~80% (Site 6) of

total extractable Ca (most of the remainder having been removed by $NaHCO_3$, and to a lesser degree by CDB), which is not all that surprising when one considers the simple reaction:

$$MgCl_2(aq.) + CaCO_3(s) \rightarrow MgCO_3(s) + CaCl_2(aq.)$$

So although $MgCl_2$ may not remove the various forms of apatite, it is to be expected that any P associated with $CaCO_3$ would be released in this phase.

Efficiency of the $MgCl_2$ extractions

The merits of carrying out repeated extractions have been demonstrated (Figure 5.3.6). However, having to carry out five repeated extractions (in a sequential scheme that itself consists of six steps) in order to remove an acceptable amount of FRP in the case of the floc sediment not only makes the whole fractionation procedure very long and cumbersome, but also increases the potential for cumulative errors. This may be partially responsible for the low percentage of total sediment P recovered by the scheme from the floc (Table 1, Appendix 5.1). Increasing the extractant:sediment ratio would have the disadvantage of not having enough sediment for following steps in the sequence. Further research is required to find a more suitable reagent (e.g. comparison with NH_4Cl, NaOAc, etc.) to more efficiently extract this P pool from sediments with high P content.

5.4.2 $NaHCO_3$ and NaOH extracts

Considering the organic nature of the sediments, it is not surprising that most of the extractable P in both sediment types was organically bound. Even in less organic-rich sediments and surface waters, it has been found that most of the total P is in an organic phase (Wetzel, 2001). This is presumably because the reactive phases are quickly taken up by the biota and hence, in the absence of anthropogenic inputs, tend not to accumulate. As in the present study, other P partitioning studies of organic sediments have also found that the largest P pool by far was the NaOH-extractable (Nieminen & Pentilä, 2004; Paludan & Jensen, 1995), the majority of this being organic P. In Baldwin's (1996b) study of the sediment P composition of 10 waterbodies (natural and man-made), $NaHCO_3$ extracted between 20% and 60% of total sediment P, with the natural wetlands having the higher values. Unlike in the present study, though, P_{NaOH} was always lower than P_{NaHCO_3}. This could be because the sediments were not as organic as the ones studied by Paludan and Jensen (1995) or Nieminen and Pentilä (2004), or the ones in the present study.

In the scheme used, two organic pools, $NaHCO_3$- and NaOH-extractable, were distinguished. A $NaHCO_3$ leach was inserted before the CDB leach in order to remove organic matter (and associated P) which the CDB leach would otherwise remove (Baldwin 1996a). Since $NaHCO_3$ is the weaker reagent, it can be assumed that it extracts the more labile components of the organic matter. A weaker version of this reagent (i.e. 0.5 M) is routinely used in the soil sciences to estimate plant available P (Kuo, 1996; Olsen, Cole, Watanabe, & Dean, 1954), and hence this phase can be considered to be relatively easily mineralisable. According to Olsen et al. (1954) however, in calcareous, alkaline and neutral soils this reagent also extracts P from calcium phosphates by decreasing the concentration of Ca^{2+} ions in solution (through precipitation of $CaCO_3$), and this decrease enhances the dissolution of Ca-phosphates. In acid soils the high pH of the reagent (8.5) causes the release of P from Al- and Fe-phosphates such as variscite ($AlPO_4.2H_2O$) and strengite ($FePO_4.2H_2O$). Since the extracts contained varying quantities of all of the elements in question (including 13% - 41% of total extractable Fe –Appendix 5.1), it is not possible to determine exactly the source/sources of this P pool. This is particularly so because slightly acid soils (pH 6-7) can contain both Ca- and Al-, as well as Fe phosphates (Olsen et al., 1954). Nevertheless, it is clearly essential to include a $NaHCO_3$ leach before the CDB leach because all the Fe_{NaHCO_3} would otherwise have been leached by CDB, and wrongly interpreted as 'bound to Fe oxides/hydroxides'.

Determining the source of the P_{NaOH} is no easier because different authors extract it at different stages in their respective schemes, use different molarities (0.1 M being the most common), and give different definitions. For example, Nieminen and Penttilä (2004; who used the method of Chang & Jackson, 1957), after removing 'easily soluble' and 'Al-bound', refer to this fraction as 'Fe-bound'. Williams et al. (1971) refer to it as 'Al bound P', Paludan and Jensen (1995), after removing Fe-bound P with CDB, refer to it as 'dissolved reactive P sorbed to clay minerals and oxides of Al, together with a major part of organic P'. The latter authors acidified an aliquot of the NaOH extract and the P in the precipitated humic acids was interpreted as 'humic acid P'. Baldwin (1996b) found good correlations of NaOH extracted P and phospholipid concentrations (but not with any of the co-extracted metals). He suggested (after undertaking ^{31}P n.m.r. analysis) that the NaOH fraction consisted in part of polyphosphates likely to be of bacterial origin. Golterman et al. (1998) questioned this conclusion, however, because of analytical problems associated with ^{31}P n.m.r. spectroscopy, and the toluidine blue method used is not specific for the identification of

polyphosphates. They determined that the NaOH extracts contained (in addition to Fe-bound P) phytate (inositol hexaphosphate) and humic phosphates. The significance of this is that phytate-P can be released from sediments under anaerobic conditions (Suzumura & Kamatani, 1995).

Given the strong humic colour of these extracts in the present study, it is very likely that much of the extracted P was associated with humic and fulvic acids. The fact that between 15% and 25% of total extractable Al (compared to between 3% and 15% in the CDB extracts) was co-extracted, and high FNRP was associated with high Al and high gilvin in the wet sediments (see Figures 1 and 2 in Appendix 5.3), suggests the presence of Al-P-humic complexes in these extracts (at least in the wet sediments). Organic P consists of, among other things, P contained in living cells, and this appears to be extractable with NaOH (Baldwin 1996b). One might therefore expect that drying would decrease the amount of NaOH-extractable P, because of the death/destruction of the living cells (from bacteria, etc.), and increase the more labile organic pools, such as P_{NaHCO_3}. However, what in fact occurred in both sediment types (although to varying degrees) was the opposite. Drying increased the P_{NaOH} and decreased the P_{NaHCO_3} pool (see Figure 5.3.2). One explanation for this could be that the degradation of organic matter (including that contained in living cells) brought about by drying made these compounds more easily extractable with this reagent. This is supported by the decrease in the size of the non-extractable portion of P in the dried sediments. It is well known that drying enhances the solubility of humic compounds (Fierer and Schimel, 2002; Kaiser & Zech, 1999; Simonsson, Berggren, & Gustafsson, 1999; Zsolnay et al., 1999). The reason why these substances remained in the NaOH pool and did not shift to the $NaHCO_3$ could be that they remained as relatively non-reactive P, whereas P_{NaHCO_3} is much more easily mineralisable (Olsen et al., 1954).

Efficiency of the $NaHCO_3$ and NaOH extractions

The comments made above regarding the efficiency of the $MgCl_2$ extractions also apply to the $NaHCO_3$ extractions. However, because gilvin in the last extractions were reduced to very low levels (see Figure 3a in Appendix 5.5), it can be assumed that the majority of this P pool was recovered. The same cannot be said about the NaOH extracts. In these extracts, there was no correlation between FRP and gilvin, but there were positive relationships between FNRP and gilvin in the wet sediments (Figure 1 in Appendix 5.3). It is suspected the lack of a positive relationship between these two variables in the dried sediments is due to the lower pH of the Site 6 sediments. Because

drying resulted in a greater pH decline, humic substances are adsorbed more strongly than in the Site 3 sediments, where the pH after drying was higher (Chapter 4). This also explains why more FNRP could be extracted with NaOH from the dried Site 6, than from the dried Site 3 sediments (i.e. because of the already mentioned competition of humic substances with phosphate for adsorption sites).

Since gilvin in the second (and last) NaOH extracts were still very high (especially compared to those in the $NaHCO_3$ extracts – compare Figures 3 and 5 in Appendix 5.5), there is a high probability that organic P (and hence TFP) in the samples was underestimated. This, together with the unavoidable cumulative errors resulting from the many repeated extractions and steps involved, could be the main reason for the relatively poor P recovery rate by the scheme. For organic sediments, it would be better therefore for P extraction efficiency to be guided by the amount of total P in the extracts, rather than FRP. However, this would be rather impractical due to the need for digestion of the samples prior to analysis.

5.4.3 CDB extracts

This reagent extracts P bound to easily reducible Fe-oxides (both amorphous and crystalline; Ruttenberg, 1992). The notion that it extracts only Fe-bound P has been challenged since Fe and Al are closely associated (Salcedo & Medeiros, 1995). CDB did extract between ~3% and 15% of total extractable Al. The fact that drying decreased the amount of CDB-extractable TFP in both sediment types may again be an indication of increased P sorption capacity. However, while drying decreased P_{CDB}, it actually increased Fe_{CDB} and Al_{CDB}. The increase in Fe_{CDB} may be because of the oxidation of pyrite-Fe to amorphous Fe (oxy)hydroxides (De Groot and Fabre, 1993); and the increase in Al_{CDB} is consistent with Simonsson et al.'s (1999) finding that drying increases Al solubility. The only metal co-extracted with P that decreased as a result of drying was Mn (Appendix 5.1, Table 3).

Nevertheless, it can be concluded that P_{CDB} in the sediments investigated was insignificant, compared to other pools, and hence does not warrant further discussion. One point must be mentioned though. The scheme extracted only between ~16% and 47% of total Fe. This is because, as shown in Chapter 6, a large proportion of Fe was $KClO_3$-extractable (i.e. bound to organics and sulfides). If any P was associated with this pool then, the scheme used in this study would be unable to extract it. However, it is highly unlikely that any P would be associated with this pool (apart from the

'organics' which would have been extracted by NaOH in the present scheme) because once Fe forms pyrite, it cannot adsorb P (Caraco et al., 1993).

Comparison of Fe_{CDB} and 0.25 M NH_2.OH.HCl-Fe + 1.0 M NH_2.OH.HCl-Fe (Chapter 6) revealed that CDB extracted similar amounts of Fe as 0.25 M NH_2.OH.HCl + 1.0 M NH_2.OH.HCl (Table 5.4.1). Given the enormous difficulty of analysing P in the CDB extracts due to potential sulfide formation and matrix interferences, it may be better to use the latter reagents which are not only easier to analyse (allowing for distinction between FRP and FNRP) but also distinguish between P bound to amorphous and P bound to crystalline iron oxides (Hall et al., 1996).

Table 5.4.1:

Comparison of Fe and Al extracted with CDB (buffered citrate-dithionate) and with 0.25 M NH_2.OH.HCl + 1.0 M NH_2.OH.HCl (mg g^{-1} sediment oven-dry basis). Note that both reagents extracted similar amounts of Fe but the latter extracted much more Al.

	Fe		**Al**	
Sample	**0.25 M NH_2 + 1 M NH_2**	**CDB**	**0.25 M NH_2 + 1 M NH_2**	**CDB**
Wet peat (Site 3)	1.79	1.82	0.76	0.16
Wet peat (Site 6)	4.49	3.50	0.81	0.23
Dry peat (Site 3)	1.96	2.12	0.62	0.27
Dry peat (Site 6)	3.74	3.73	0.57	0.42
Wet floc (Site 3)	0.68	0.37	1.17	0.07
Wet floc (Site 6)	0.73	0.85	0.90	0.09
Dry floc (Site 3)	1.05	0.90	1.06	0.16
Dry floc (Site 6)	0.99	0.94	0.76	0.13

5.4.4 HCl and Ashing/HCl extracts

The very low levels of P_{HCl} in the sediments are similar to Baldwin's (1996b) study where very low levels of P_{HCl} in the sediments of 10 Australian water bodies were also found. Apparently Australian freshwater sediments typically have a low incidence of apatite. However, as discussed in 5.4.2, there is the small possibility that any apatite that may have been present would have been removed with $NaHCO_3$.

The ashing/HCl pool consists mainly of organic/refractory organic P (Baldwin 1996a; Ruttenberg 1992). The relatively high proportions of this P pool confirms the

incomplete NaOH extraction discussed above. As in the NaOH leach, the comparatively high levels of both P and Al in the extracts suggest the presence of humic-Al-P complexes. If the ashing/HCl P and the non-extractable P pools are considered to be mainly organic P, then, together with the $NaHCO_3$ and NaOH pool, ~84% (wet) and ~92% (dried) of the total P extracted from the peat was organically bound, and ~77% (wet) and 50% (dried) of the total P extracted from the floc was organically bound.

5.4.5 Dissolved humic colour

The effectiveness of the 1 M NaOH, compared to the $NaHCO_3$ and the CDB reagents in extracting humic substances was evident. However, as discussed in 5.4.2, gilvin was not completely extracted because the second extracts still contained large amounts of colour, particularly the dried peat samples. The fact that more humic colour in total was extracted from Site 3 than from Site 6 (even though both sites had virtually the same percentage of LOI), demonstrates that, just as P is more strongly sorbed on acidic sediments (see discussion in 5.4.2), so are humic compounds, presumably for the same reasons (hence the competition for sorption sites). Also, even though there was only very slightly less organic matter in the floc than in the peat (LOI peat 78.6% and 78.1%, floc 73.1% and 70.1% for Sites 3 and 6 respectively), significantly less gilvin was extracted from the floc (Table 7, Appendix 5.1). This suggests that the floc organic matter is less humified (i.e. consists of lower molecular weight fractions) and by extension is more labile (Wetzel, 2001). This difference is probably a reflection of the different organic matter origins in the peat and floc (e.g. phytoplankton vs. vascular plants; see Chapter 3), and/or may be in a different state of decomposition.

In spite of these likely differences in the nature and source of OM, drying increased the amount of extractable gilvin from both sediment types demonstrating the enhanced solubility of humic compounds resulting from drying. The fact that the CDB extracts contained any gilvin at all implies that this reagent must have extracted some organic matter, in spite of the prior $NaHCO_3$ leach. There is the possibility that Fe in these extracts may have absorbed at 440 nm, however there were no correlations between Fe and gilvin in any of the CDB extracts (Appendix 5.3), so this is not very likely.

Given the relatively large difference in gilvin content between peat and floc, it is somewhat surprising that the E_4:E_6 ratios of the individual extracts were quite similar. The relatively low ratios (overall) indicate the presence of higher molecular mass type organic matter (i.e. probably more humic than fulvic acids) and also a relatively high

degree of aromaticity. A ratio of <~5 generally indicates the presence of more humic acids and >~5 the presence of more fulvic acids (Chen et al., 1977). The increase in the ratios as a result of drying, particularly in the peat $NaHCO_3$ and NaOH extracts indicate an increase in the incidence of lower-weight DOC. This would not only increase bioavailability to bacteria, but also decrease the sediment sorption capacity for these humic acids. Vermeer & Koopal (1998) have shown that bigger humic acid molecules displace faster sorbing smaller fulvic acids in a slow process. However, in the floc, the effect of drying was inconclusive, because the ratio in the $NaHCO_3$ extracts decreased while it increased slightly in the NaOH extracts. A decrease in the E_4:E_6 ratio would indicate condensation to bigger compounds (Chen et al., 1977). The higher ratios measured in the CDB extracts of the dried peat samples could simply mean that the lower molecular weight substances (i.e. fulvic acids) were more easily extractable with CDB.

The analysis of gilvin in the soil extracts appears to have provided more useful information than the E_4:E_6 ratios (which were just a preliminary attempt at using a proxy to characterise DOC in the extracts). Obviously, much more experimental work (e.g. using n.m.r. and other techniques) is required if we are to understand the nature of organic matter in aquatic sediments, let alone how drying affects these.

5.4.6 Comparison with incubation data

Based on a summation of the $MgCl_2$-FRP, $NaHCO_3$-FRP and CDB-P fractions, the percentages of total sediment P potentially available for photosynthesis in the short to medium time scale would be ~25% and ~23% in the wet peat (Sites 3 and 6 respectively), ~17% and ~19% in the dried peat, ~33% and ~29% in the wet floc, and ~56% and ~57% in the dried floc. Even though there were relatively large amounts of non-extractable residual P, these percentages can be considered to be relatively accurate, because the proportion that could not be chemically extracted would unlikely be reactive or bio-available. Comparison with the incubation data presented in Chapter 4 (see also Appendix 5.4) shows that in fact, with the exception of the dried floc, less than these values were released on the 7^{th} day of incubation (when the highest P concentrations in the incubations were measured). Closer examination of the Site 3 data (Appendix 5.4) reveals that ~73% more P was released under anaerobic conditions from the dried than from the wet peat. This might seem inconsistent with the extraction data which strongly suggest that drying increased P sorption capacity of the peat. However this is not necessarily the case because even though more P was mobilised from the

dried sediments, this still was less than the total amount of P that could be potentially released. An increase in P sorption *capacity* of the sediment does not mean P will sorb more strongly, if the biogeochemical environment does not allow for this to happen (i.e. strongly reducing). Comparison with the aerated treatments further illustrates this point. Here, in spite of drying-induced increased mineralisation of P, similarly low amounts of P were released from the wet and dried/rewet peat treatments (see Figure 4.3.8, Chapter 4 and this chapter Appendix 5.4), and by Day 49 the wet aerated treatments had slightly higher P concentration than the dried/rewet aerated treatments. In the case of the Site 6 peat data, ~35% less P was released from the dried/rewet than from the wet anaerobic incubations on Day 21 (when the highest P concentration in this incubation was measured). This represents only a small proportion of the total P potentially releasable (namely ~7%, compared to ~60% in Site 3). Site 6 was the only site of a total of six from Lake Goollelal that released less P from the dried/rewet than from the wet peat under anaerobic conditions (Chapter 4). As discussed in 5.4.1, this difference is probably due to differences in sediment characteristics, mainly pH, Fe and Ca concentration and the Fe:P ratio.

Given the large total P concentration in the floc, and that ~⅓ of this was potentially mobilisable (based on the fractionation data), the very low concentration of TFP in the wet anaerobic incubations, especially when compared to the wet peat anaerobic incubations, is intriguing (see Appendix 5.4). Although it is to be expected that much more P will be displaced by a strong reagent such as 1M $MgCl_2$ compared to natural conditions in a wetland, it is still surprising that more P was released from the wet peat than from the wet floc under anaerobic conditions, given the much higher P concentration of the floc, and also the fact that EC (i.e. ionic strength) was twice as high in the floc slurries than in the peat slurries. Comparison of fractionation data, physico-chemical data in the incubations and sediment elemental composition between the floc and peat, provides no insight as to why this might be. A small clue is provided though by the fact that there was virtually no difference between the amount of P mobilised from the aerated and anaerobic wet floc incubations (both were negligible). This suggests that P cycling in the (wet) floc may not be redox-dependent. One plausible explanation for this may be that, although, as has been shown, a good proportion of total P is *chemically* extractable with $MgCl_2$ or NaOAc (and is therefore chemically reactive), *physically* this P may not be mobilisable under normal aquatic physico-chemical conditions. It is possible that P is physically 'trapped' within the floc structure. Another possibility is that the high water content of flocs discourages osmotic diffusion

into the surrounding water. These observations could explain why P concentration in the surface water of Lake Goollelal is low compared to the high sediment concentration. Given the extent and depth of the suspended flocculated layer at Lake Goollelal (see Chapter 3), this is a massive P sink, taking up both P released from the peat below and any water column P. Not only is it a massive P sink, it is probably also a very stable P sink (Wilkinson & Reinhardt, 2005). Childers et al.'s (2003) suggestion that marsh dry-down is the primary mechanism by which floc becomes part of the consolidated sediment can be supplemented by the findings of the present study. Only a very insignificant proportion (i.e. ~0.33% based on Sites 3 and 6, see Appendix 5.4) of total potentially mobilisable P was actually mobilised in the incubation experiments (Chapter 4). This suggests that, not only is drying the primary mechanism by which floc becomes part of the consolidated sediment, but drying/reflooding is also the primary mechanism by which P can be released from the floc structure. Presumably this is because drying destroys the floc structure (of which water is a major component). As with the wet floc, P release from the dried/rewet floc appeared to be largely (although not entirely) redox-independent since significant release occurred under both anaerobic and aerobic conditions (Appendix 5.4).

There was a discrepancy between the amount of P released from the dried/rewet floc incubations and the calculated maximum mobilisable P from the fractionation study. On Day 7, 72% and 76% (Sites 3 and 6 respectively) of total sediment P was released from the dried/rewet anaerobic incubations, while maximum potentially mobilisable P calculated from the fractionation study was 56% and 57%. This discrepancy may be partly because analysis of such high concentrations of FRP requires high dilution rates of the samples. Small inaccuracies are then multiplied by the dilution factor which can amount to a big difference in the end. Another contributing factor could be that some of the P released from the dried/rewet floc originated from different P fractions, e.g. the NaOH pool. Suzumura and Kamatani (1995) found that, despite being chemically refractory, phytate (shown to be extractable with NaOH – Golterman et al., 1998) was effectively mineralised to inorganic P by aerobic and anaerobic degradation processes. This creates an interesting situation. While chemically labile P is not mobilisable from the wet floc, chemically refractory P is mobilisable from the dried/rewet floc under the same environmental conditions. This highlights the importance of comparing P fractionation data with field observations and/or P release studies. In order to improve the P extraction efficiency of NaOH it would probably also

be advisable to carry out the extractions under anaerobic conditions (since phytate is mainly released anaerobically).

There is another mechanism by which P can be released from the floc. In the Site 6 aerated wet incubation the pH between Day 35 and 49 declined from 3.8 to 2.6 which coincided with an additional release of 430 μg L^{-1} of TFP. However, even under such extreme acidic conditions, this still only represented 0.68% of total floc P. Therefore, acidification is probably a minor P release mechanism from these flocs, compared to drying/reflooding.

5.5 Conclusions

Sequential fractionation of organic sediments from Lake Goollelal has shown that there were important differences in the amounts and partitioning of P between the two sediment types, peat and suspended floc, and also between dried and undried samples. In the peat, ~84% of total sediment P was organically bound. Drying decreased P_{MgCl_2}, P_{NaHCO_3} and P_{CDB} (the potentially mobilisable P fractions), and this was interpreted as being due to increased P sorption capacity of the sediment. At the same time there was a substantial increase in P_{NaOH} and $P_{ashed/HCl}$. Along with analysis of dissolved humic colour in the extracts, this was interpreted as being evidence for drying-induced increase in solubility of humic matter and associated P.

In the (wet) floc 77% of total sediment P was organically bound. In contrast to the peat, drying substantially increased P_{MgCl_2}, however this was not interpreted as being due to a decrease in sediment affinity for P because when P (in the form of pyro-phosphate, Table 8 in Appendix 5.1) was added to floc samples, the dried sediments retained considerably more P than the wet sediments. In addition, drying decreased the P_{NaHCO_3} and P_{CDB} pools in the floc, suggesting increased P binding capacity. In this case the most likely reason for the increase in P_{MgCl_2} was the very high P content compared to Fe (and Al) content in the floc. There was probably not enough of these (oxy)hydroxides to sorb the large quantities of P derived from the organic P fractions (especially when considering that most of the Fe in the floc was bound up with sulfides). As in the peat, drying increased the solubility of humic matter (measured as $gilvin_{440}$) although humic colour in the floc was markedly less than in the peat. This was probably a reflection of the different source, and/or degree of decomposition of the organic matter in the two sediment types.

Comparison with the incubation data presented in Chapter 4 revealed that, with the exception of the dried floc, much less TFP was released than potentially mobilisable under anaerobic conditions. Nevertheless, ~¾ more TFP was released from the dried peat of one of the sites, in spite of the apparent increase in sediment P affinity. The reason for this was probably that the reducing conditions in the anaerobic slurries did not promote adsorption. In the more acidic site, however ~⅓ less TFP was released under anaerobic conditions from the dried/rewet than from the wet peat. This was attributed mainly to the low pH, and much higher Fe:P ratio of the sediments from this site.

Negligible amounts of TFP were released from the wet anaerobic floc incubations despite the fact that, based on P fractionation, ~⅓ of total sediment P (which was 7 times higher than in the peat) was potentially mobilisable. No explanation for this could be found in the fractionation data, nor in the elemental composition of the floc. Because there was virtually no difference between the amount of TFP released from the wet anaerobic and wet aerated incubations (and only a small difference in the dried treatments), it was concluded that P release from the floc must be largely redox-independent. It was proposed that the comparatively large proportion of reactive P in the floc, although chemically labile, must be physically trapped within the floc structure. By contrast, ~20% more P than potentially mobilisable (as calculated from the fractionation data) was released in the dried/rewet floc anaerobic treatments. Apart from possible inaccuracies due to high dilution rates, it is possible that in addition to the calculated potentially releasable P, chemically refractory P (potentially phytate-derived P) was released.

This study has shown that, despite its inherent drawbacks, sequential fractionation of P can provide useful information about P partitioning in organic aquatic sediments, however interpretation of the results can be complicated. There are also implications for P fractionation studies of organic sediments. Drying of organic sediments results in better overall P-extractability, however, this obviously has a significant impact on P partitioning. The scheme used, the SEDEX scheme (Ruttenberg 1992) as adapted by Baldwin (1996b) for (Australian) organic sediments, can be improved by: (1) increasing the extractant to sediment ratio for ‘adsorbed/loosely bound P’ where high P concentrations are expected (such as in the floc of the present study) in order to reduce the number of repeated extractions necessary; (2) replacing the CDB leach with a 1.0 M NH_2.OH.HCl leach; apart from the analytical benefits, this would

also allow for the determination of co-extracted S in the extracts; (3) in the NaOH leaches, use humic colour in the extracts as a guide for removal efficiency, and fractionate the DOC in the leaches (e.g. using the techniques described in Paludan and Jensen 1995); also carry out this leach anaerobically in order to be able to better extract phytate P; (4) omitting the HCl leach (because of the negligible amount of P recovered by this reagent). Additional information regarding the nature of organic P could be obtained by applying techniques such as n.m.r. (nuclear magnetic resonance) spectroscopy and other techniques (e.g. those discussed in Golterman, 1998). A knowledge of total sediment elemental composition (in the very least P, Fe, Al, Ca and S), as well as organic matter type and content, is essential before selection of appropriate extraction techniques. In addition, this study has shown that information about P partitioning as provided by a sequential extraction procedure is in itself not sufficient for predicting P release from aquatic sediments. It is important to supplement such investigations with laboratory P-release experiments and/or field observations. Consideration of sediment characteristics such as pH and mineralogy will also greatly assist the interpretation of P partitioning in organic sediments.

CHAPTER 6
ELEMENTAL FRACTIONATION OF WET AND DRIED AQUATIC PEAT AND FLOC SEDIMENTS FROM LAKE GOOLLELAL, WESTERN AUSTRALIA

Abstract

In this chapter, the effects of desiccation, as distinct from oxidation, on the sulfidic, organic sediments of Lake Goollelal were investigated. An elemental extraction scheme (Hall et al., 1996) was used to identify elemental geochemical phases in wet and air-dried peat and suspended floc. The dominant iron and sulfur phases (representing between 70% to 90% of both total sediment Fe and S) were potassium chlorate ($KClO_3$)-extractable (i.e. bound to organics and sulfides), and approximately half of this amount was chromium-reducible (i.e. pyrite, monosulfides, acid volatile and elemental sulfur). The 'free' amorphous iron pool (0.25 M hydroxylamine extracts) in both sediment types was very small, and the crystalline iron pool (1 M hydroxylamine extracts) virtually non-existent (even after drying). The dominant calcium pool was sodium acetate (NaOAc)-extractable (most likely calcium carbonate). This pool represented only a fraction of that required to neutralise the acidity which could potentially be produced by the S_{KClO_3} pool.

The main conclusion of the study was that drying *per se* would not bring about acidification, since drying did not appreciably reduce the oxidisable iron and sulfur pools in either sediment type (in fact, it increased in the floc). Oxidation during the drying process would have reduced Fe_{KClO_3} and S_{KClO_3}, and increased these elements in either one or more of the NaOAc, 0.25M- or 1M NH_2.OH.HCl pools. The reason the sediments did not oxidise appreciably during the drying, is that they went more or less straight from an anaerobic state into the drying oven. The main impacts of drying on the sediments investigated were an increase in Ca_{NaOAc} (i.e. adsorbed/exchangeable/ carbonate), and a decrease in Fe_{NaOAc} (most likely due to organic coatings formed upon drying) in both sediment types. It can be assumed that other organic-rich wetlands on the well-buffered Spearwood dunes on the Swan Coastal Plain (currently suffering from declining water levels) have similar high levels of oxidisable S as Lake Goollelal, since they formed under similar circumstances. Not all of them have a nutrient-rich organic floc layer which would potentially buffer against drought-induced acidification. Where

the peat layer is deep, the underlying limestone lithology is essentially isolated from the surface layers, and would therefore not be available for buffering. The considerable amounts of acidity likely to be produced, not by drying but by oxidation of the sediments due to low water levels, would very likely override the buffering potential provided by the alkaline groundwater feeding these wetlands.

6.1 Introduction

Global climate change and poor water resource management practices have led to increasing instances of drought-induced acidification of inland surface waters world-wide (e.g. Lamers, Vanroozendaal et al., 1998; Lucassen et al., 2002; Sommer & Horwitz, 2001; Van Haesebroeck et al., 1997). Acidification can severely impact the ecology of surface waters, and also has the potential to pollute groundwater resources on which humans rely (Appleyard et al., 2004). In the Northern Hemisphere atmospheric acid deposition has exacerbated the sensitivity of such wetlands to drought (Lamers, Vanroozendaal et al., 1998; Lucassen et al., 2002). On the Swan Coastal Plain of Western Australia atmospheric acid deposition is not an issue; nevertheless, in the last few decades several wetlands have suffered intermittent or permanent acidification (McHugh, 2004; Sommer & Horwitz, 2001). In some cases this was supposedly triggered by mining of peat and diatomaceous earths, which exposed and oxidised pyritic sediments. In most instances however the acidification trends coincided with gradually decreasing groundwater levels in the superficial aquifer.

All of the thus affected wetlands are located on the poorly-buffered geomorphic unit called the Bassendean dunes. This is the oldest (Pleistocene), most easterly, lowest and most leached of a series of dune systems that make up the Swan Coastal Plain (Figure 1.1, Chapter 1). To the west of the Bassendean dune system are the siliceous Spearwood dunes which overlie limestone, and adjacent to the coast are the calcareous Quindalup dunes, the youngest unit (McArthur & Betteney, 1960). The majority of the wetlands which occur either within or between the dune systems are hydraulically connected to the superficial aquifer and thus lake water levels reflect the groundwater table (Davidson, 1995). Likewise, surface water quality largely reflects groundwater quality, with the Bassendean wetlands tending to be coloured, base-poor and slightly acidic, while wetlands on the Spearwood and Quindalup dunes tend to be richer in calcium carbonate with relatively high to very high pH.

As with the Bassendean wetlands, the Spearwood wetlands have also been experiencing lower water levels and extended periods of drought during the past few

years. Thanks to good buffering capacities, however, none of these, until very recently, have suffered from acidification events. At the time of writing, there is grave concern that some of the organic-rich Spearwood wetlands are experiencing pH declines (e.g. Lake Wilgarup, Lake Mariginiup, Lake Gwelup). Organic sediments (peat) are particularly susceptible to acidification upon exposure because they can contain large stores of pyrite. This is especially so for peats that have had some form of marine influence during their paleohistory (Dellwig et al., 2002), such as those on the SCP. High sulfate input from sea water, combined with high iron and ample organic matter from terrestrial sources favour sulfate-reducing bacterial activity, creating conditions that are very conducive to pyrite formation (Giblin & Wieder, 1992). Indeed, pyritic peaty soils are not uncommon within the Spearwood dunes (Teakle & Southern, 1937). This has recently become an issue when the drainage, excavation and stockpiling of sulfide-rich peat soils for urban development caused widespread groundwater acidity and arsenic contamination in a suburb located 5 km north of the Perth CDB, and on the otherwise well-buffered Spearwood unit (Appleyard et al., 2004).

This incident raises the suspicion, should the regional groundwater table continue to fall, that the organic-rich wetlands on the Spearwood dunes may be under threat of acidification, despite their alkaline and well-buffered geological setting. Acidification results from the oxidation of previously buried sulfide minerals and proceeds according to the following chemical equations (after Singer & Stumm, 1970):

$$FeS_2+7/2O_2+H_2O\rightarrow Fe^{2+}+2SO_4^{2-}+2H^+ \quad (6.1)$$

$$Fe^{2+}+¼O_2+H^+\rightarrow Fe^{3+}+ ½H_2O \quad (6.2)$$

$$Fe^{3+}+ 3H_2O\rightarrow Fe(OH)_{3(s)}+3H^+ \quad (6.3)$$

$$FeS_2+7Fe_3(SO4)_3+8\ H_2O\rightarrow 15FeSO_4+8H_2SO_4 \quad (6.4)$$

Equation (6.4) shows the reduction of ferric iron by pyrite itself, where sulfide is again oxidised releasing acidity, along with additional ferrous iron which may re-enter the reaction cycle via equation (2). In calcareous soils and sediments, decreases in pH are buffered by dissolution of calcium carbonate:

$$CaCO_3+H^+\Leftrightarrow Ca^{2+}+HCO_3^- \quad (6.5)$$

$$HCO_3^- + H_2O\Leftrightarrow H_2CO_3 + OH^- \quad (6.6)$$

Obviously the efficiency of this buffering effect against sulfide oxidation will depend on the amount of protons released and the amount of bicarbonate ions produced. For instance, Lucassen et al. (2002) found that desiccation led to severe acidification of a mire in the Netherlands when the sediment S: (Ca+Mg) ratio exceeded 2:3. It is also

evident from the above equations that the pH-buffering capacity of a soil or sediment will decrease as $CaCO_3$ dissolves because the Ca^{2+} ions can be washed down-stream or lost through groundwater flow (van den Berg & Loch, 2000). As the above equations suggest, it is the oxidation of the sediment and resulting buffering responses that determine whether a sediment or water body will acidify or not. They give no indication as to how drying *per se* affects these processes. In fact, although Lucassen et al. (2002) concluded that 'desiccation led to severe acidification', no attempt was made to distinguish between the effects of the actual 'desiccation' and oxidation upon rewetting. There is a wealth of literature from the soil sciences field on how drying affects soil physical and chemical properties (see Chapter 2). However, the same cannot be said about wetland sediments, especially not organic, sulfidic ones.

In addition, research into the effects of water-level changes, and indeed also of acid deposition (Shanley, Kram, Hruska, & Bullen, 2004), on alkaline wetlands and catchments has been sparse. This is probably primarily because research funding has tended to focus on base-poor systems, since this is where the bulk of acidification problems have been occurring in the past. With climate change and ever-increasing human population growth being ongoing global issues, the demands on global water resources can only intensify in the future (Zektser, 2000). In order to more fully appreciate the processes involved in drought-induced acidification, and to be able to relate these to sediment properties, it is imperative that the distinction between drying and oxidation effects is made. Despite its inherent drawbacks (Chao, 1984; Rapin et al., 1986; Ruttenberg, 1992), selective extraction schemes are a useful tool in providing information on binding sites of elements. They help in the understanding of geochemical processes, and also allow one to predict the potential for remobilisation and bioavailability of an element (Hall, Vaive, Beer et al., 1996).

In this study the elemental extraction scheme of Hall et al. (1996) was used to identify the elemental speciation of the organic sediments of a wetland fed by alkaline and iron-rich groundwater and investigate the effects of drying on these. The focus was on the key elements iron, sulfur and calcium, however co-extracted manganese, aluminium and silicon were also evaluated. A previous study (Chapter 4) described the geochemical processes that took place when the same organic sediments were air-dried and reflooded, distinguishing between the effects of aerobic (aerated) and anaerobic conditions. The aim of the present study was to determine the effect of desiccation on the elemental distribution of different geochemical phases, but specifically on the

oxidisable sulfur fraction. In other words, if in the incubation study an acidification response was observed, was this due to drying-induced changes in the sediments themselves, or was this exclusively due to oxidation? A secondary aim was to determine, should a desiccation effect be established, whether the effect will be the same in two different sediment types, peat and overlying suspended organic floc. Finally, the fractionation results were compared with observed transformations of chemical species in the incubation study described in Chapter 4.

6.2 Materials and methods

6.2.1 Study site, sample collection and preparation

The study site, sample collection and preparation methodologies have been previously described (Chapter 3). A detailed characterisation of the Lake Goollelal sediments is also given in Chapter 3. The fractionation scheme described below requires a large number of steps (including repeated extractions in order to ensure more thorough removal of individual phases) and replicates, and hence, due to limited time and resources not all of the sediment samples used in the incubation study (Chapter 4) could be fractionated. Peat and floc samples from two locations (known to have high sediment sulfur and iron concentration – see Chapters 3 and 4) were therefore selected from the eastern side of the lake (Sites 3 and 6 – see Figure 3.1.1b, Chapter 3) and analysed for two treatments – dried and wet (= two sites x two sediment types x two treatments x 3 replicates x 6 phases; plus multiple extractions and blanks). Sediment sub-samples from the same sites were also used for a phosphorus fractionation study (Chapter 5).

6.2.2 Elemental fractionation and laboratory methods

Sequential fractionation involves a series of successive chemical treatments of a sample, each being more drastic in action, or of a different nature, than the previous one. Numerous such schemes exist (a number of them are reviewed in Hall et al., 1996); ultimately it was decided that the sequential extraction scheme described in Hall et al. (1996) would be best suited to the nature of the sediments in this study. This is mainly because: (1) it does not involve Tamm's reagent (0.175 M ammonium oxalate in oxalic acid at pH 3.2 in the dark) which was found to be non-selective in the presence of organic complexes (Hall et al., 1996), (2) there is differentiation between amorphous and crystalline forms of iron, and (3) it does not involve the commonly used citrate-dithionite buffer ("CDB" or "DCB") for the extraction of crystalline iron oxides which Hall et al. (1996) found to have numerous flaws including formation of sulfides and

being highly contaminated. In addition, included in the scheme is a step aimed at dissolving sulfide minerals which was of particular interest in this study.

The procedure used is shown schematically in Figure 6.2.1. It deviates from the scheme described in Hall et al. (1996) in the following ways. Instead of 1g sample being used, 0.5 g of dried sample was used. Less was taken because of the expected high iron concentrations (see Chapter 3). The wet samples were first centrifuged (under anoxic conditions) to remove porewater, then approximately 4 g (exact weight recorded) of this was weighed into 50-ml *Falcon* centrifuge tubes that had been preflushed with ultra high-purity N_2 gas. More of the wet than of the dry sediment was used to take into account water content. Subsamples of the wet and air-dried sediment were oven-dried at 105°C in order to determine equivalent oven-dry weights. A 0.1 M sodium pyro-phosphate extraction (pyro-P) was inserted after the 1 M sodium acetate (NaOAc) extraction because of the organic nature of the sediments. This extracts elements bound to humates and fulvates (Hall & Pelchat, 1997). In the last step an *aqua regia* digestion (Chen & Ma, 2001) instead of HF-$HClO_4$-HNO_3 was used to extract residual elements. This was done because our laboratory was not equipped to handle hazardous hydrofluoric acid. After each extraction, samples were rinsed with 10 ml Milli-Q water (Hall et al. used 5 ml). All phases were double-extracted, apart from the 1 M $NH_2OH.HCl$ phase, which was extracted three times (because a strong yellow colour was still evident in the second leachate), and the $KClO_3$ phase, which was extracted only once. All extractions were carried out in triplicate and blanks were run throughout the procedure. The leachates, after appropriate dilution (see Figure 6.2.1), were analysed for aluminium (Al), silicon (Si), sulfur (S), calcium (Ca), manganese (Mn) and iron (Fe) by inductively coupled plasma – atomic emission spectroscopy (ICP-AES) at the Marine and Freshwater Research Laboratory at Murdoch University, Perth.

6.2.3 Statistical analyses

General descriptive and explorative statistics were mainly used to describe the data (because n was equal to two [i.e. two sites, 3 and 6], the three replicate samples being 'pseudo-replicates'). Correlation-based principal component analyses (Primer for Windows Package (v. 5.2.1)) were used (using the means of the three replicate extractions; n=8) to summarise patterns of (normalised) elemental distribution and treatment effects (i.e. dry/wet; peat/floc). This type of analysis is particularly useful for the ordination of environmental data. Its aim is to find a set of orthogonal vectors in the data space that accounts for as much of the data variance as possible. The data are

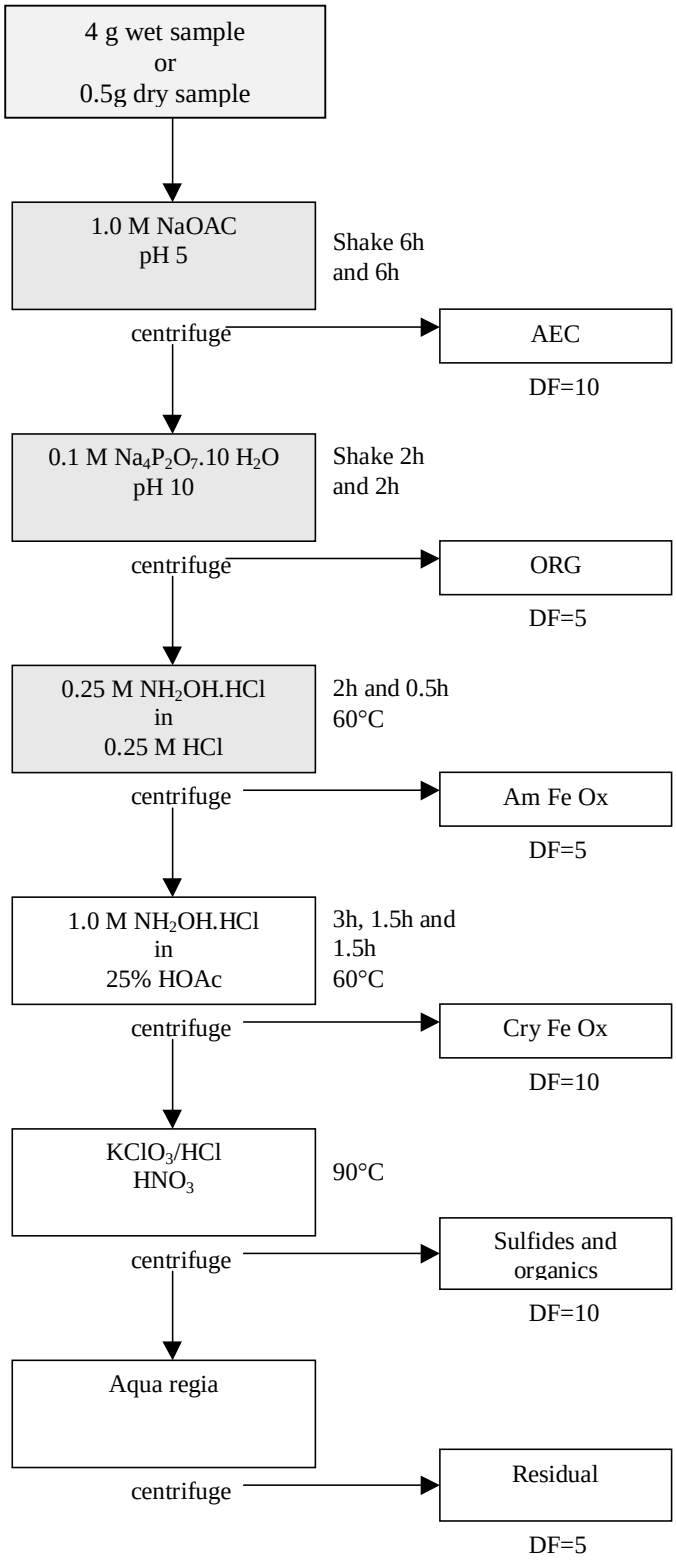


Figure 6.2.1: Schematic of the sequential extraction procedure modified after Hall et al. (1996). AEC=adsorbed/exchangeable/carbonate; ORG=bound to humates and fulvates; Am Fe Ox=amorphous Fe oxyhydroxides; Cry Fe Ox=crystalline Fe oxide; DF=dilution factor prior to analysis. Shaded boxes indicate that extraction was carried out under anoxic conditions.

projected from their original multi-dimensional space (representing the full set of environmental variables, or principal components) onto a reduced-dimensional subspace spanned by these vectors which should retain most of the intrinsic information in the data. The first principal component axis shows the direction in which the variance of sample points projected perpendicularly onto the axis is maximised. The second principal component is constrained to lie in the subspace perpendicular to the first. Within that subspace, it points in the direction of the maximum variance. Then, the third principal component (if any) is taken in the maximum variance direction in the subspace perpendicular to the first two, and so on. In Primer, a correlation matrix is produced and this was used to detect the strength of relationships between variables. Two-way crossed ANOSIM was used to detect if there were any significant differences between treatment and sediment types, however, again because n was equal to only two, these differences were not significant. More details, including algorithms used, can be found in Clarke & Warwick (1994).

6.3 Results

The graphs in Figure 6.3.1 show mean elemental distributions of wet and dried peat and floc sediments as determined by sequential extraction. Standard errors (n=3) and a mass balance of the sequential analyses are given in Tables 1-7 in Appendix 6.1. Please also refer to sediment characteristics in Chapter 3.

6.3.1 Sodium acetate extracts

Sodium acetate ('adsorbed/exchangeable/carbonate') extracted markedly less Fe from all of the dried sediments, than from the wet ones, although this was only a small portion of total Fe (Figure 6.3.1). For Sites 3 and 6 respectively, means of 0.82 and 3.39 mg g^{-1} (equivalent to 2.97% and 6.44% of total extractable Fe) was extracted from the wet peat, and 0.03 and 2.10 mg g^{-1} (0.11% and 5.46%) from the dried peat; and 1.60 and 3.10 mg g^{-1} (6.59 and 5.89%) from the wet floc, and 0.05 and 0.21 mg g^{-1} (0.16 and 0.34%) from the dried floc. Mn_{NaOAc} was the dominant Mn phase in the peat, and unlike with Fe_{NaOAc}, drying increased this. For Sites 3 and 6 respectively, 0.015 and 0.010 mg g^{-1} (53.94% and 59.40% of total extractable Mn) was extracted from the wet peat, and 0.018 and 0.013 mg g^{-1} (57.90% and 66.61%) from the dried peat.

Drying decreased the amount of Al_{NaOAc} from the Site 3 peat (by 63.9%), but in the Site 6 peat this increased (by 29.1%). In the floc of both sites drying increased Al_{NaOAc} considerably (by 100% and 372% for Sites 3 and 6 respectively). For Sites 3

and 6 respectively, 0.130 and 0.299 mg g^{-1} (3.94 and 8.23% of total extractable Al) was extracted from the wet peat, and 0.047 and 0.386 mg g^{-1} (1.59% and 11.39%) from the dried peat; and 0.029 and 0.179 mg g^{-1} (0.63% and 4.92%) from the wet floc, and 0.058 and 0.844 mg g^{-1} (1.18 and 20.92%) from the dried floc.

As with Mn, Ca_{NaOAc} was also the dominant Ca phase in both sediment types, and drying increased this by an average of 22% in the peat and by 10% in the floc. For Sites 3 and 6 respectively, 12.51 and 5.96 mg g^{-1} (75.46% and 76.88% of total extractable Ca) was extracted from the wet peat, and 15.41 and 7.94 mg g^{-1} (85.60% and 87.02%) from the dried peat; and 12.18 and 7.64 mg g^{-1} (78.10% and 78.10%) from the wet floc, and 14.04 and 8.27 mg g^{-1} (87.87% and 87.10%) from the dried floc (Figure 6.3.1). S_{NaOAc} from the two sites responded differently to drying. In Site 3, the response was similar to that of Fe, i.e. drying decreased the amount of S extractable in both sediment types (by 56.9% in the peat and by 17.9% in the floc). In Site 6, drying increased the amount of S_{NaOAc} (by 218.6% in the peat and by 47.2% in the floc). Compared to Site 3, there was very little S_{NaOAc} in the wet samples (both peat and floc) at Site 6. For Sites 3 and 6 respectively, 4.36 and 0.59 mg g^{-1} (11.08% and 1.06% of total extractable S) was extracted from the wet peat, and 1.88 mg g^{-1} (4.48% and 4.05%) from the dried peat of both sites; and 1.96 and 0.56 mg g^{-1} (5.37% and 0.89%) from the wet floc, and 1.61 and 0.98 mg g^{-1} (3.73% and 1.31%) from the dried floc (Figure 6.3.1). Only a very small portion of total sediment Si was extracted by the scheme. NaOAc extracted more Si from the wet than from the dried samples, as did the majority of the other extractants (see Figure 6.3.1).

The principal component analysis (PCA) for the NaOAc extractions shows a clear division between wet and dry treatments (Figure 6.3.2). Within these two major groupings, there appears to be more similarities between sediments from the same site, than between sediment type. The first principal component, which explains 56.6% of total variance, was primarily driven by Mn and Ca (i.e. increasing Mn and Ca concentrations along the x-axis), followed by Fe (decreasing concentrations along the x-axis). Correspondingly, there were significant inverse relationships between Fe and Ca ($r= -0.773$, $p<0.012$, $n=8$) and between Fe and Mn ($r= -0.765$, $p<0.014$, $n=8$; see Appendix 6.2). The second principal component was driven primarily by Si (i.e. increasing concentration of Si up the y-axis; raw PCA results in Appendix 6.3).

6.3.2 Sodium pyro-phosphate extracts

The results for the pyro-phosphate ('bound to humates and fulvates') extracts were varied. Pyro-P extracted more Fe from all of the dried than from the wet sediments, apart from the Site 3 peat (where the opposite was the case). For Sites 3 and 6 respectively, 3.43 and 5.79 mg g^{-1} (12.38% and 10.99% of total extractable iron) was extracted from the wet peat, and 1.33 and 6.21 mg g^{-1} (5.50% and 16.15%) from the dried peat; and 0.76 and 0.83 mg g^{-1} (3.13% and 1.58%) from the wet floc, and 1.23 and 3.70 mg g^{-1} (4.40% and 3.70%) from the dried floc (Figure 6.3.1). $Mn_{pyro\text{-}P}$ and the following two phases ($Mn_{0.25M\ NH_2.HCl}$ and $Mn_{1M\ NH_2.HCl}$) were very small, and therefore analytically unreliable. It is hence not possible to ascertain the effects of drying on these phases.

Apart from residual Al, $Al_{pyro\text{-}P}$ was the dominant Al phase in the peat, but not in the floc. Drying decreased $Al_{pyro\text{-}P}$ in the peat of both sites, and in the floc of Site 6, while in the Site 3 floc this was about the same in both the wet and dried floc. For Sites 3 and 6 respectively, 0.852 and 0.918 mg g^{-1} (25.88% and 25.29% of total extractable Al) was extracted from the wet peat, and 0.703 and 0.867 mg g^{-1} (23.54% and 25.579%) from the dried peat; and 0.449 and 0.395 mg g^{-1} (9.73% and 10.86%) from the wet floc, and 0.451 and 0.304 mg g^{-1} (9.14% and 7.54%) from the dried floc (Figure 6.3.1).

Although small compared to Ca_{NaOAc}, $Ca_{pyro\text{-}P}$ represented the second largest Ca phase, and drying decreased this in all samples. For Sites 3 and 6 respectively, 2.62 and 0.97 mg g^{-1} (15.78% and 12.53% of total extractable Ca) was extracted from the wet peat, and 2.07and 0.89 mg g^{-1} (11.52% and 9.71%) from the dried peat; and 2.08 and 1.36 mg g^{-1} (13.31% 13.94%) from the wet floc, and 1.52 and 0.96 mg g^{-1} (9.48% and 10.09%) from the dried floc (Figure 6.3.1). There was more $S_{pyro\text{-}P}$ in all of the dried than in the wet sediments. For Sites 3 and 6 respectively, 1.89 and 1.46 mg g^{-1} (4.82% and 2.61% of total extractable S) was extracted from the wet peat, and 2.46 and 2.10 mg g^{-1} (5.82% and 4.52%) from the dried peat; and 1.77 and 1.83 mg g^{-1} (4.85% and 2.92%) from the wet floc, and 2.37 and 2.21 mg g^{-1} (5.49% and 2.96%) from the dried floc (Figure 6.3.1).

The inconsistent responses described above are reflected in the PCA plot in Figure 6.3.3. Unlike the NaOAc extracts, there is no clear grouping of treatment effects,

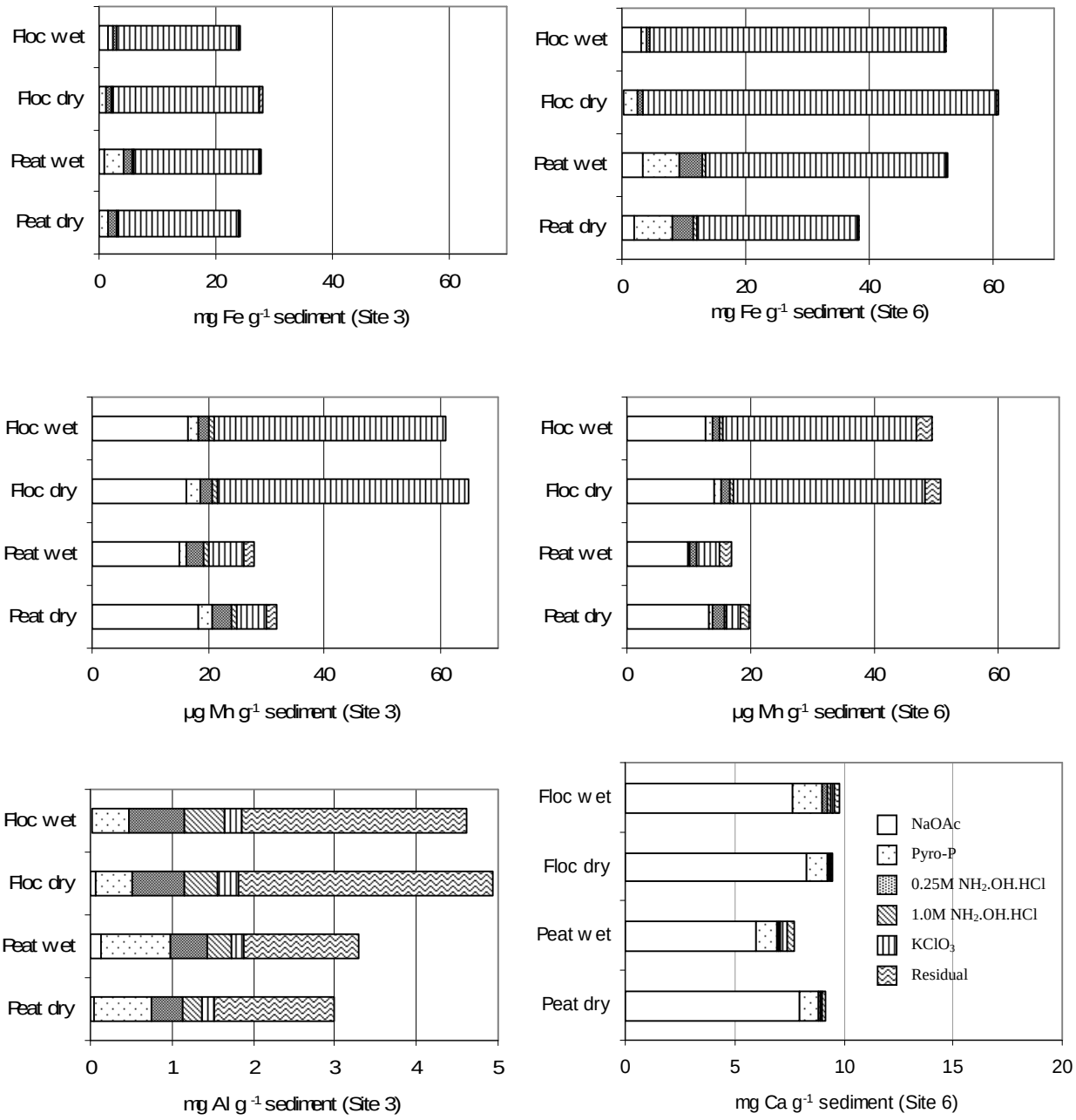


Figure 6.3.1 Elemental partitioning (mean Fe, Mn, Al, Ca, S and Si; n=3) in two sediment types from two sites (3 and 6) at Lake Goollelal. Weights are on oven-dry basis. Standard errors are given in Appendix 6.1.

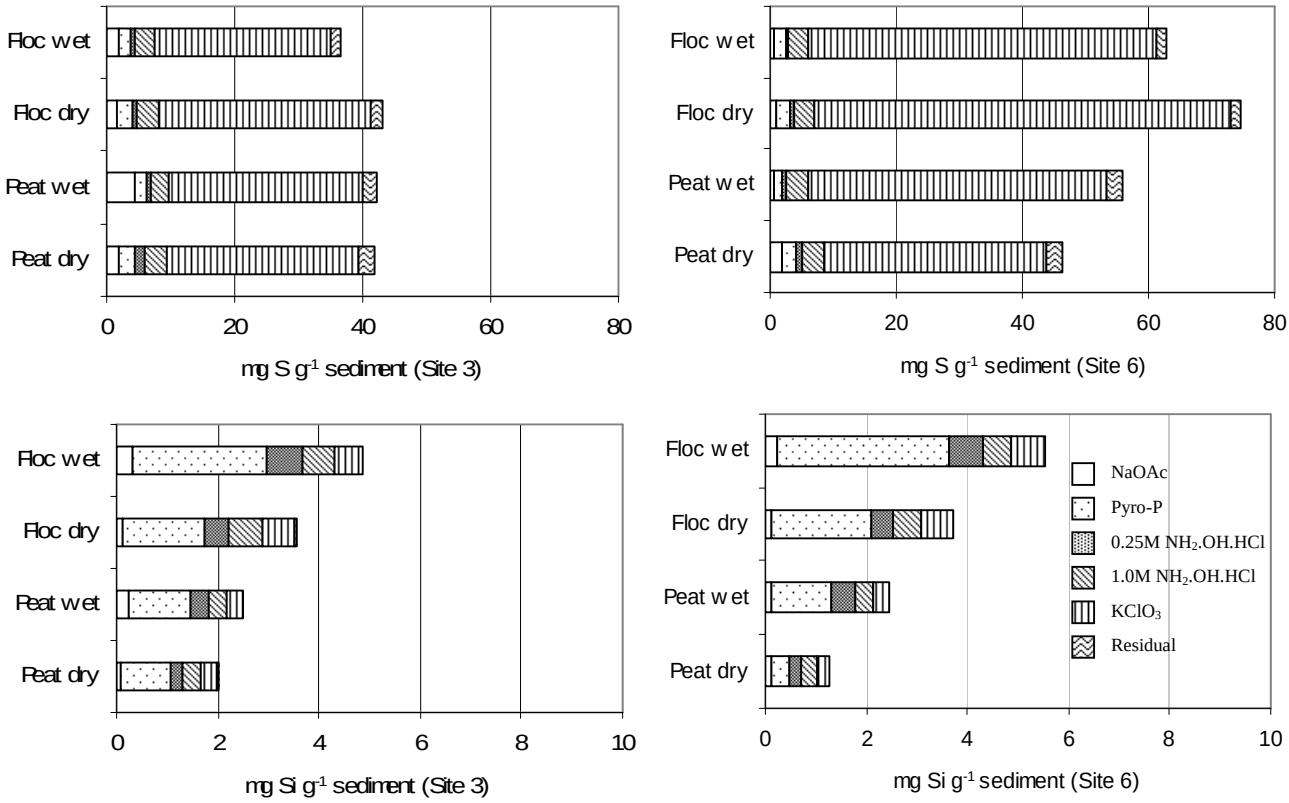


Figure 6.3.1 (cont.)

however there is a relatively good separation by sediment type, with the peat to the left and the floc to the right of the plot. This distribution (PC1 and PC2 accounting for 78.6% of total variance) reflects the higher $Fe_{pyro\text{-}P}$ and $Al_{pyro\text{-}P}$ concentrations in the peat than in the floc (decreasing concentrations of both elements along the PC1 axis).

6.3.3 0.25 M Hydroxylamine extracts

The 0.25 M hydroxylamine ('amorphous iron oxyhydroxides' and co-extracted elements) extracted more Fe from the Site 3 dried peat and floc (14.2% and 64.3% more respectively), and from the Site 6 dried floc (47% more) than from the wet sediments. However it extracted 16.1% less from the Site 6 dried peat than from the wet peat. For Sites 3 and 6 respectively, 1.55 and 3.28 mg g^{-1} (5.60% and 7.42% of total extractable Fe) was extracted from the wet peat, and 1.77 and 3.28 mg g^{-1} (7.33% and 8.51%) from the dried peat; and 0.56 and 0.57 mg g^{-1} (2.30% and 1.08%) from the wet floc, and 0.92 and 0.84 mg g^{-1} (3.29% and 1.38%) from the dried floc (Figure 6.3.1). In contrast to Fe, 0.25 M hydroxylamine extracted slightly less Al from the dried than from the wet peat and floc from both sites. For Sites 3 and 6 respectively,

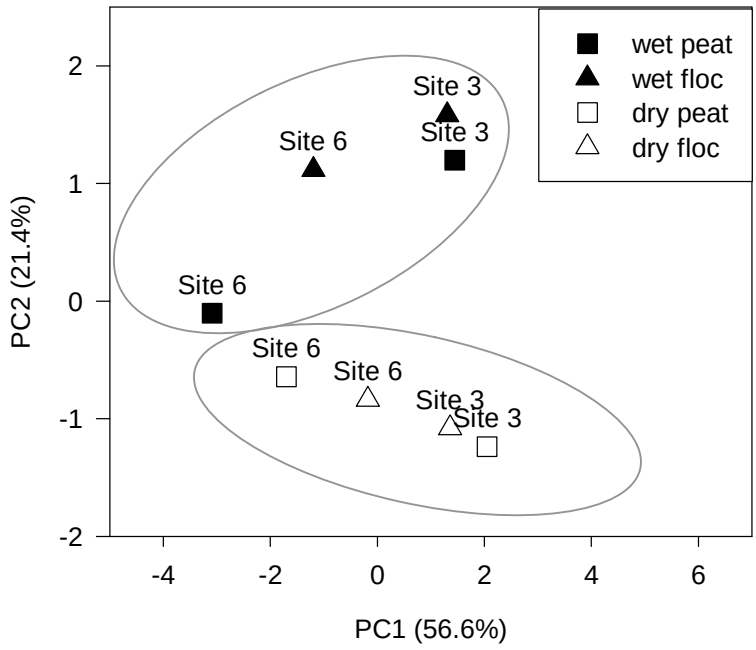


Figure 6.3.2: Two-dimensional PCA ordination of normalised elemental concentrations extracted with sodium acetate from 'wet' and 'dried' sediments ('peat' and 'floc') from two sites at Lake Goollelal (Sites 3 and 6). PC1 and PC2 account for 78% of the total variability. Solid grey lines show treatment groupings.

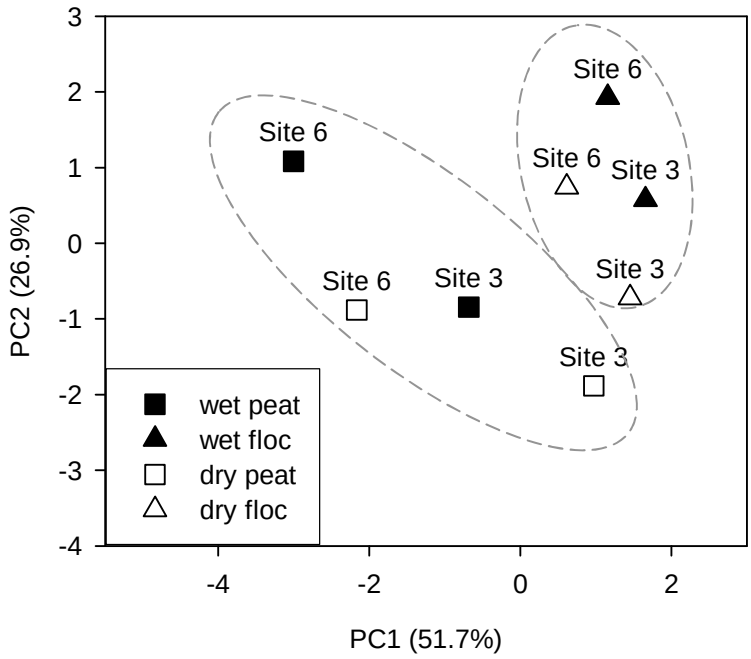


Figure 6.3.3: Two-dimensional PCA ordination of normalised elemental concentrations extracted with pyro-phosphate from 'wet' and 'dried' sediments ('peat' and 'floc') from two sites from Lake Goollelal (Sites 3 and 6). PC1 and PC2 account for 78.6% of the total variability. Dashed grey lines show sediment type groupings**.**

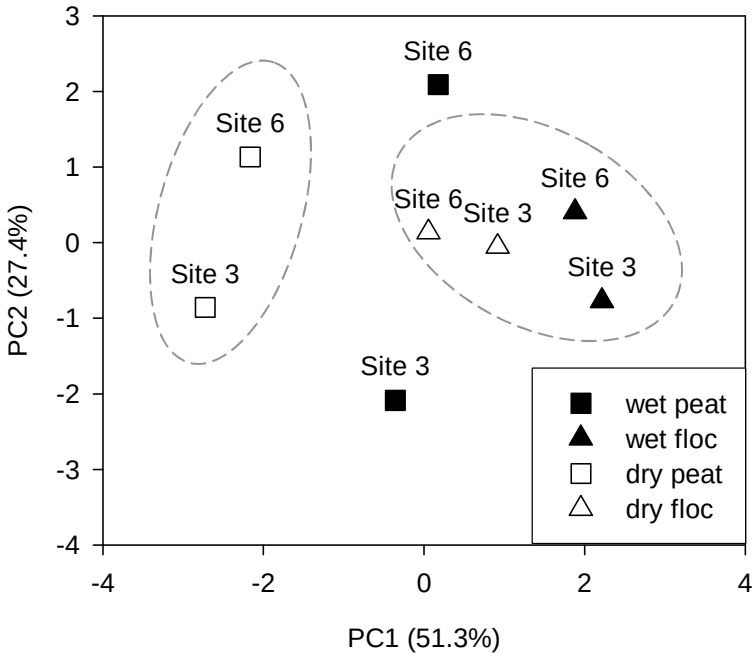


Figure 6.3.4: Two-dimensional PCA ordination of normalised elemental concentrations extracted with 0.25 M hydroxylamine from 'wet' and 'dried' sediments ('peat' and 'floc') from two sites from Lake Goollelal (Sites 3 and 6). PC1 and PC2 account for 78.7% of the total variability. Dashed grey lines show sediment type groupings.

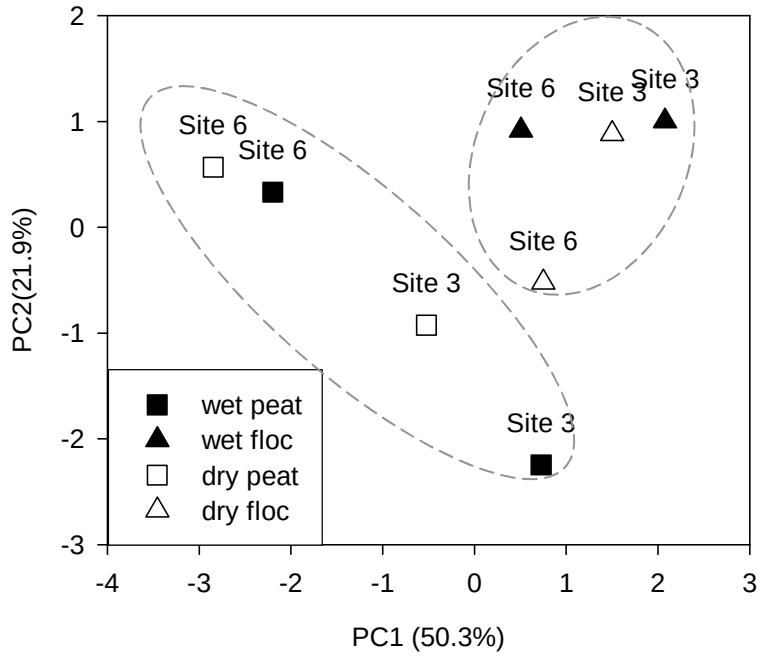


Figure 6.3.5: Two-dimensional PCA ordination of normalised elemental concentrations extracted with 1 M hydroxylamine from 'wet' and 'dried' sediments ('peat' and 'floc') from two sites from Lake Goollelal (Sites 3 and 6). PC1 and PC2 account for 72.2% of the total variability. Dashed grey lines show sediment type groupings.

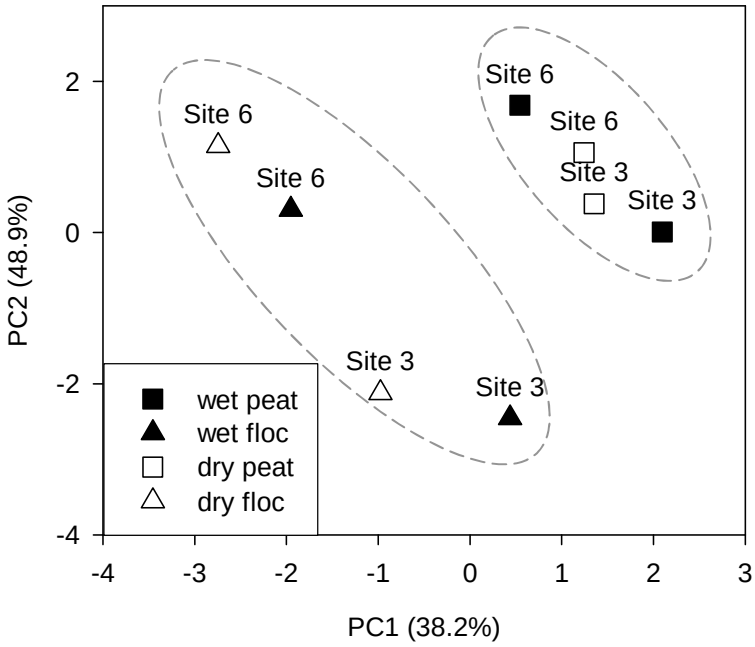


Figure 6.3.6: Two-dimensional PCA ordination of normalised elemental concentrations extracted with $KClO_3$ from 'wet' and 'dried' sediments ('peat' and 'floc') from two sites from Lake Goollelal (Sites 3 and 6). PC1 and PC2 account for 87.1% of the total variability. Dashed grey lines show sediment type groupings.

0.449 and 0.510 mg g-1 (13.63% and 14.04% of total extractable Al) was extracted by 0.25 M hydroxylamine from the wet peat, and 0.379 and 0.343 mg g^{-1} (12.70% and 10.13%) from the dried peat; and 0.668 and 0.509 mg g^{-1} (14.47% and 13.97%) from the wet floc, and 0.644 and 0.458 mg g^{-1} (13.05% and 11.36%) from the dried floc (Figure 6.3.1).

This and the following two extractants all leached less Ca from the dried than from the wet samples, these phases each representing only a very minor and insignificant portion of total extractable Ca. Although also only a minor phase of total sediment S, the amount of S co-extracted from the dried sediments was markedly higher than that extracted from the wet sediments (+ 163% and 118% for Sites 3 and 6 peat respectively; and + 49% and 60% for Sites 3 and 6 floc respectively). For Sites 3 and 6 respectively, 0.66 and 0.48 mg g^{-1} (1.68% and 0.85% of total extractable S) was extracted from the wet peat, and 1.74 and 1.05 mg g^{-1} (4.14% 2.27%) from the dried peat; and 0.49 and 0.43 mg g^{-1} (1.35% and 0.69%) from the wet floc, and 0.73 and 0.69 mg g^{-1} (1.69% and 0.93%) from the dried floc (Figure 6.3.1).

The PCA in Figure 6.3.4 shows all floc sediments grouped relatively tightly in the centre right of the ordination space. Within this group there is a further grouping

into treatment type. This is largely a reflection of the higher concentrations of Si and Al in the floc samples, and drying decreased these amounts. The first principal component, which accounted for 51.3% of total variance, was hence primarily driven by Si and Al, followed by Fe (see raw results in Appendix 6.3), while the second was driven primarily by the minor constituents Ca and Mn (i.e. increasing concentrations of Ca and Mn up the y-axis). This might not have been the case if the data had not been normalised (which gives them equal weighting), however, removal of Si, Mn and Ca resulted in very similar groupings, demonstrating the dominating role of the major constituents Fe, Al and S. The strongest correlation in the ordination was between Al and Si ($r= 0.802$, $p< 0.008$, see Appendix 6.2).

6.3.3 1 M Hydroxylamine extracts

Less Fe was extracted with the 1 M hydroxylamine ('crystalline iron oxides') than with the 0.25 M hydroxylamine (despite the fact three repeated extractions were carried out), and this was in fact the smallest Fe phase. The third extracts contained between 15%–16% of the total amount of Fe leached with 1 M hydroxylamine in the wet peat samples, 9–13% in the dried peat, 28%–30% in the wet floc and between 22%–23% in the dried floc samples. In the peat samples drying decreased the amount of extractable Fe by ~21%, while in the floc there was virtually no difference between wet and dry. For Sites 3 and 6 respectively, 0.24 and 0.58 mg g^{-1} (0.85% and 1.11% of total extractable Fe) was extracted from the wet peat, and 0.19 and 0.46 mg g^{-1} (0.80% and 1.20%) from the dried peat; and 0.12 and 0.16 mg g^{-1} (0.47% and 0.30%) from the wet floc, and 0.92 and 0.84 mg g^{-1} (0.46% and 0.24%) from the dried floc (Figure 6.3.1).

As with the 0.25 M, the 1 M hydroxylamine extracted less Al from the dried than from the wet peat and floc from both sites. For Sites 3 and 6 respectively, 0.310 and 0.299 mg g^{-1} (9.41% and 8.24% of total extractable Al) was extracted from the wet peat, and 0.237 and 0.229 mg g^{-1} (7.95% and 6.75%) from the dried peat; and 0.501 and 0.390 mg g^{-1} (10.87% and 10.72%) from the wet floc, and 0.416 and 0.299 mg g^{-1} (8.42% and 7.42%) from the dried floc (Figure 6.3.1).

1 M Hydroxylamine extracted more S than 0.25 M hydroxylamine, and also extracted more from the dried than the wet samples (unlike Fe and Al), although this was of a smaller magnitude than with the 0.25 M hydroxylamine. For Sites 3 and 6 respectively, 2.83 and 3.36 mg g^{-1} (7.21% and 5.99% of total extractable S) was extracted from the wet peat, and 3.33 and 3.61 mg g^{-1} (7.94% and 7.77%) from the dried

peat; and 3.29 and 3.34 mg g^{-1} (9.00% and 5.32%) from the wet floc, and 3.26 and 3.09 mg g^{-1} (7.55% and 4.149%) from the dried floc (Figure 6.3.1).

Only 72.3% of total variability could be explained by the first two axes in the PCA shown in Figure 6.3.5. The figure shows two poorly defined groupings into sediment type (mainly due to higher Al concentration in the floc samples), with no clear pattern in the distribution of treatment types.

6.3.4 Potassium chlorate extracts

Fe_{KClO3} (bound to 'sulfides and organics') was the dominant Fe phase in all of the samples. In the peat, drying decreased the amount of Fe extractable (although by only 3.6% in the Site 3 peat, compared to 32.4% less in the Site 6 peat), and in the floc samples drying increased this amount (by ~20% in both sites). For Sites 3 and 6 respectively, 21.42 and 38.70 mg g^{-1} (77.33% and 73.48% of total extractable Fe) was extracted from the wet peat, and 20.64 and 26.17 mg g^{-1} (85.38% and 68.02%) from the dried peat; and 20.90 and 47.60 mg g^{-1} (86.02% and 90.53%) from the wet floc, and 25.28 and 57.26 mg g^{-1} (90.16% and 93.72%) from the dried floc. S_{KClO3} was also by far the dominant S phase in all of the samples. In the Site 3 peat, drying did not have a marked effect on the amount of extractable S (0.3% less was extracted from the dried samples), however in the Site 6 peat drying decreased this amount by 26%. As with Fe, the floc samples showed the opposite response, with ~20% more S being leached from the dried, than from the wet floc samples. For Sites 3 and 6 respectively, 30.13 and 47.44 mg g^{-1} (69.03% and 84.67% of total extractable S) was extracted from the wet peat, and 30.05 and 35.11 mg g^{-1} (71.59% and 75.53%) from the dried peat; and 27.37 and 55.09 mg g^{-1} (74.84% and 87.84%) from the wet floc, and 33.20 and 66.11 mg g^{-1} (76.88% and 88.58%) from the dried floc (Figure 6.3.1). Because of the magnitude of this phase, air-dried sediment sub-samples were analysed for chromium-reducible sulfur (by the Chemistry Centre WA) according to the Acid Sulfate Soils Laboratory Methods Guidelines (Ahern et al., 2004). This method is considered to be specific for reduced inorganic sulfur compounds (pyrite, acid volatile S and elemental S; Canfield, Raiswell, Westrich, Reaves, & Berner, 1986) and therefore the difference between the two analyses is probably primarily organic S. The results are shown in Table 6.3.1, which shows that approximately twice the concentration of S was determined with the $KClO_3$ extraction than with the chromium reduction method.

Table 6.3.1:

Cr-reducible sulfur and sulfur extracted with $KClO_3$ and HCl followed by 4 M HNO_3 of two sediment types from two locations at Lake Goollelal (oven-dry basis). Both analyses were carried out on air-dried samples.

Site	Sediment type	Cr-reducible S (%)	$KClO_3$ extract (%)	Difference (%)
3	Peat	1.46	3.01	1.55
	Floc	1.55	3.32	1.77
6	Peat	1.45	3.51	2.06
	Floc	4.04	6.61	2.57

The floc contained markedly more Mn_{KClO_3} than the peat, and this was in fact the dominant Mn phase in the floc. However, drying had no marked effect on these concentrations (nor did it in the peat – Figure 6.3.1; see also Table 2, Appendix 6.1). Drying increased Al_{KClO_3} concentration in both peat samples and the Site 3 floc, but in the Site 6 floc drying slightly decreased this. For Sites 3 and 6 respectively, 0.142 and 0.114 mg g^{-1} (4.30% and 3.15% of total extractable Al) was extracted from the wet peat, and 0.157/0.147 mg g^{-1} (5.27/4.35%) from the dried peat; and 0.217 and 0.157 mg g^{-1} (4.70% and 4.32%) from the wet floc, and 0.243 and 0.150 mg g^{-1} (4.93% and 3.72%) from the dried floc.

The PCA plot in Figure 6.3.6 clearly groups the samples into sediment types, and into sites within these groups, rather than treatment type, reflecting the lack of impact of drying on this phase. The large amounts of Fe and S extracted in this phase is reflected in the high percentage of variability explained by the first and second principal components, viz. 87.1% (Figure 6.3.6). On Figure 6.3.6, Fe and S increase upwards along the PC2 axis, and downwards along the PC1 axis. Fe and S were highly significantly correlated ($r= 0.998$, $p< 0.000$, $n=8$, see Appendix 6.2).

6.3.5 Aqua regia extracts, and comparison of totals extracted by the scheme with total sediment concentrations

Aqua regia leached the 'residual' amounts of the various elements. For Sites 3 and 6 respectively, the residual amount of Fe that could be extracted with *aqua regia* was small with 0.24 and 0.30 mg g^{-1} (0.87% and 0.56% of total extractable Fe) from the

wet peat, and 0.22 and 0.25 mg g^{-1} (0.89% and 0.65%) from the dried peat; and 0.36 and 0.33 mg g^{-1} (1.48% and 0.62%) from the wet floc, and 0.43 and 0.37 mg g^{-1} (1.53% and 0.61%) from the dried floc. In total (i.e. all phases combined), the scheme extracted less Fe from the dried than from the wet peat, but more Fe from the dried than from the wet floc. For Sites 3 and 6 respectively, 27.70 and 52.66 mg g^{-1} was extracted from the wet peat, and 24.18 and 38.47 mg g^{-1} from the dried peat; and 24.29 and 52.58 mg g^{-1} from the wet floc, and 28.03 and 61.09 mg g^{-1} from the dried floc. For Sites 3 and 6 respectively, 96.8 and 89.9% of total sediment Fe as determined by XRF (see Chapter 3) was extracted from the wet peat, and 82.1% and 65.7% from the dried peat; and 81.8% and 81.0% from the wet floc, and 94.4% and 94.1%) from the dried floc.

For Mn, for Sites 3 and 6 respectively, 0.006 and 0.004 mg g^{-1} (21.11% and 21.54% of total extractable Mn) was extracted from the wet peat, and 0.005 and 0.002 mg g^{-1} (16.73% and 11.16%) from the dried peat; and 0.040 and 0.031 mg g^{-1} (61.98% and 63.67%) from the wet floc, and 0.043 and 0.031 mg g^{-1} (62.86% and 61.31%) from the dried floc. In total, the scheme extracted more Mn from the dried than from the wet peat and floc. For Sites 3 and 6 respectively, 0.028 and 0.017 mg g^{-1} was extracted from the wet peat, and 0.032 and 0.020 mg g^{-1} from the dried peat; and 0.065 and 0.049 mg g^{-1} from the wet floc, and 0.069 and 0.051 mg g^{-1} from the dried floc. For Sites 3 and 6 respectively, 84.88% and 80.26% of total sediment Mn as determined by ICP after acid digestion (Chapter 3) was extracted from the wet peat, and 96.36% and 94.33% from the dried peat; and 72.72% and 98.77% from the wet floc, and 77.43 and 102.72%) from the dried floc.

Drying had no marked effect on the amount of Al extractable by aqua regia from any of the samples, and this was easily the largest Al phase. For Sites 3 and 6 respectively, 1.41 and 1.49 mg g^{-1} (42.84% and 41.05% of total extractable Al) was extracted from the wet peat, and 1.46 and 1.42 mg g^{-1} (48.94% and 41.80%) from the dried peat; and 2.75 and 2.01 mg g^{-1} (59.60% and 55.22%) from the wet floc, and 3.13 and 1.98 mg g^{-1} (63.30% and 49.05%) from the dried floc. In total, the scheme extracted less Al from the dried than from the wet peat, but more from the dried than from the wet and floc. For Sites 3 and 6 respectively, 3.29 and 3.63 mg g^{-1} was extracted from the wet peat, and 2.99 and 3.39 mg g^{-1} from the dried peat; and 4.61 and 3.64 mg g^{-1} from the wet floc, and 4.94 and 4.03 mg g^{-1} from the dried floc. For Sites 3 and 6 respectively, 102.81% and 88.58% of total sediment Al as determined by XRF analysis

was extracted from the wet peat, and 93.31% and 82.65% from the dried peat; and 78.21% and 79.19% from the wet floc, and 83.68% and 87.70%) from the dried floc.

In total, the scheme extracted more Ca from the dried than from the wet peat, and also slightly more from the Site 3 dried than from the wet floc, but slightly less from the Site 6 floc. For Sites 3 and 6 respectively, 16.58 and 7.76 mg g^{-1} was extracted from the wet peat, and 18.00 and 9.12 mg g^{-1} from the dried peat; and 15.60 and 9.78 mg g^{-1} from the wet floc, and 15.97 and 9.49 mg g^{-1} from the dried floc. Total sediment Ca was 2.5 times higher in the Site 3 than in the Site 6 peat, and 1.4 times higher in the Site 3 than in the Site 6 floc. For Sites 3 and 6 respectively, 84.59% and 102.07% of total sediment Ca as determined by XRF analysis was extracted from the wet peat, and 91.86% and 120.06% from the dried peat; and 92.31% and 82.19% from the wet floc, and 94.53% and 79.76% from the dried floc.

There was slightly more 'residual' S in the dried than the wet samples. For Sites 3 and 6 respectively, 2.43 and 2.70 mg g^{-1} (6.18% and 4.82% of total extractable S) was extracted from the wet peat, and 2.52 and 2.73 mg g^{-1} (5.99% and 5.87%) from the dried peat; and 1.68 and 1.47 mg g^{-1} (4.60% and 2.34%) from the wet floc, and 2.01 and 1.55 mg g^{-1} (4.66% and 2.08%) from the dried floc. Total sediment S was ~1.2 times higher in the Site 6 than in the Site 3 peat, and ~1.5 times higher in the Site 6 floc, than in the Site 3 floc. For Sites 3 and 6 respectively, 76.77% and 91.42% of total sediment S as determined by analysis on a Leco analyser was extracted from the wet peat, and 81.97% and 75.84% from the dried peat; and 69.53% and 82.85% from the wet floc, and 82.11% and 98.59% from the dried floc.

Not surprisingly, only a very small portion of total sediment Si was extracted by the scheme. The majority of extractants extracted more Si from the wet than from the dried samples (Figure 6.3.1, also Table 7 in Appendix 6.1). Exceptions are the 1M hydroxylamine extracts from the Site 3 floc, and the $KClO_3$ extracts from both the Site 3 peat and floc, where slightly more Si was extracted from the dried, than from the wet samples. Total sediment Si was ~1.3 times higher in both the Site 6 peat and floc than in the Site 3 sediments. For Sites 3 and 6 respectively, only 6.42% and 5.037% of total sediment Si as determined by XRF analysis was extracted from the wet peat, and 5.16% and 2.61% from the dried peat; and 8.39% and 7.795% from the wet floc, and 6.15% and 5.25%) from the dried floc.

6.4 Discussion

Before commencing this discussion it is essential to recognise that the phases extracted by any sequential extraction scheme are 'operationally defined' (Hall et al. 1996), and are by no means 100% selective. This means that some quantities of each phase will inevitably be present in the preceding and subsequent extractions.

6.4.1 Sodium acetate extracts

In summary, the most important aspects of the NaOAc leach was that less Fe could be extracted from the dried than from the wet samples, and that it contained the dominant Ca pool of both wet and dried samples of both sediment types.

NaOAc extracts exchangeable (held through electrostatic attraction on exchange sites), adsorbed, carbonates and metals co-precipitated with carbonates. It extracted less Fe from all of the dried, than from the wet sediment samples. This was particularly marked for the Site 3 peat and both floc samples, where drying reduced NaOAc-extractable Fe by an average of 95%. This was unlikely the result of drying-induced increased crystallization since the 1 M hydroxylamine extractions did not point in this direction (see Section 6.4.4). Both aerated and anaerobic incubations of the same sediment samples resulted in less Fe initially being released from the dried than the continuously wet samples (Chapter 4). It was hypothesized that organic coatings (analogous to those responsible for water-repellence in terrestrial soils and sediments) formed upon drying were responsible for this. The fact that NaOAc extracted less Fe from all of the dried than from the wet sediments supports this hypothesis, since this extractant does not dissolve organic matter to any notable degree (Hall, Vaive, Beer et al., 1996).

Unlike Fe, there was (very slightly) more Mn_{NaOAc} in the dried, than in the undried samples, suggesting possible co-precipitation with $CaCO_3$, since there was also more Ca_{NaOAc} in the dried, than in the undried samples. In both the wet and dried peat samples from both sites, this (possibly $MnCO_3$, or $(Mn)CaCO_3$) was the dominant Mn phase. The inverse relationship between Fe and Mn in this phase may further suggest competition between the two elements for adsorption sites (with Fe out-competing Mn). However, in the floc there was a larger proportion of Mn_{KClO_3} (see Section 6.4.4) than Mn_{NaOAc}. The fact there was more Ca in the dried than in the undried extracts suggests that Ca (-carbonate) particles may not have been 'coated' by organic acids. This is conceivable given that $CaCO_3$ particles are usually larger (>1μm) than, say, Fe or Al

(oxy-) hydroxides, and so do not form colloids, but rather act as bridging polymers in the aggregation of colloids (Buffle, Wilkinson, Stoll, Filella, & Zhang, 1998; Stumm & Morgan, 1996). The different behaviour of Ca, compared to Fe and Al, in response to drying may also possibly be related to different mechanisms of binding between the alkaline earth and the transition metals (Hering & Morel, 1988). Since all of the following leaches contained less Ca in the dried than in the wet peat, it is possible that drying transformed Ca in the various other pools to a more labile form. For example, drying may have resulted in the breakdown and release of biologically-bound Ca (e.g. from algae or the remains of microcrustacea).

Al_{NaOAc} was only a minor proportion of total Al in the sediments (as determined by XEF), however in the Site 6 peat and in both floc samples, drying increased this amount which would equate to an increased potential for Al solubility. In terrestrial soils, drying has been shown to increase the solubility of Al (specifically of imogolite-type materials, e.g. $Al_2SiO_3(OH)_4$), and Simonsson, Berggren, & Gustafsson (1999) suggest that this is because soil organic matter is disrupted, thus exposing formerly coated mineral surfaces. Where drying did not increase the solubility of Al, they suggested that solubility was controlled by Al-humus complexes. It is therefore possible that this was the case in the Site 3 peat, where drying slightly decreased Al_{NaOAc}. Because of the highly organic nature of the sediments in the present study, it could be expected that Al would be mainly controlled by Al-humus complexes. Differences in the responses of the two peat sites were probably related to differences in sediment characteristics such as higher Al concentration and lower pH in the Site 6 peat (see Chapter 3).

The inconsistent results in terms of S_{NaOAc} between the two sites (i.e. drying decreased S_{NaOAc} in the Site 3 sediments, while it increased it in the Site 6 sediments) may indicate differences in the reactivity of mineral surfaces between the two sites (and may also be a reason why Al response to drying differed in the peat of the two sites). This is likewise most probably related to differences in sediment characteristics, particularly pH. Comfort, Dick, & Baham (1991) found that sulfate adsorption capacity increased by as much as 320% when dried soils were compared with field-moist samples; soils high in amorphous minerals, in exchangeable acidity and in total carbon were affected most. Simonsson et al. (1999, citing Karltun and Gustafsson, 1993) suggested that, since sulfate adsorption takes place on oxide surfaces rather than in soil

organic matter, drying-induced changes in sulfate sorption capacity is related to changes in the reactivity of mineral surfaces in the soil after drying.

6.4.2 Sodium pyro-phosphate extracts

The most relevant aspects of this leach were that this was the dominant *extractable* phase of both Al and Si, and that at least twice as much Fe (and Al) was extracted from the peat than from the floc. The effects of drying on the elements in this phase were by and large inconclusive.

Sodium pyro-phosphate reportedly extracts metals bound to humic and fulvic complexes. The peat samples contained a larger proportion of Fe and Al associated with this phase than did the floc samples, which again points to differences in the type/source of organic matter between the two sediment types (Chapter 3). The Fe and Al graphs in Figures 6.3.1 also suggest an overall difference in response to drying between the peat and floc samples (particularly with regards to Fe). If drying forms coatings of humic and fulvic acids on mineral surfaces (as suggested in Chapter 3), one would expect pyro-P to co-extract more metals from the dried, than from the undried samples. However, this was only clearly the case for Fe in the floc samples, but not consistently in the peat. Moreover, less Al, Ca and Si were extracted from most of the dried (peat and floc) samples than from the wet ones. There are many possible reasons for this inconsistency. One is that this extractant leaches not only adsorbed (e.g. as coatings), but also metals organically bound by other mechanisms, such as complexation and chelation (Hall, 1996). It is possible that in the cases where less metals were co-extracted from the dried, than from the wet samples, drying resulted in these metals being more firmly bound/coated by a more recalcitrant type of organic matter (perhaps altered by drying) that could not be extracted with Pyro-P. Perhaps samples were not extracted for long enough, or the reagent was too weak. Although Hall, Vaive, & MacLaurin (1996) found that the conventional leaching time of 16 h (McKeague, Brydon, & Miles, 1971) could be decreased to 1 h without significantly decreasing the amounts of Co, Cu, Fe, I, Pb and Zn extracted, their experiments were carried out on dried samples (lake sediments, 40% LOI) only. The fact more S was extracted from all of the dried than the wet samples may indicate the presence of –thiol functional groups in the organic coatings, or in other humic substances, or that drying transformed some of the organic S into more recalcitrant humic acids.

6.4.3 Hydroxylamine extracts

In summary, both the 'free' amorphous and the crystalline Fe pools in both sediment types were negligibly small, with no indication of drying-induced increase in crystallinity.

Both the weaker 0.25 M, and the stronger 1 M hydroxylamine extracts represented only minor phases of all of the elements investigated. As with the pyro-P extractant, 0.25 M hydroxylamine leached more Fe, but less Al, Ca and Si from the dried than from the undried floc samples, while the peat results for the two sites again differed for Fe, but as with the floc less Al, Ca and Si were extracted from the dried than from the wet samples. It is possible that there may have been some carry-over of humic acids from the previous leach to account for this similarity. For the 1 M hydroxylamine the overall tendency was for slightly less of all the elemental constituents being able to be extracted from the dried than from the wet samples. Two conclusions can be drawn from these observations. Firstly, the amount of 'free' amorphous ($Fe(OH)_3.nH_2O$) and crystalline iron oxides and associated metals in the sediments investigated is negligible compared to the total sediment concentration of these elements. Although selective elemental fractionation of aquatic organic sediments is rare, these results should not be surprising. Because of the high scavenging capacity of organic compounds for metals, one would expect most of these to be bound to organic matter, rather than be 'free'. Secondly, there was no indication of the often-reported drying-induced increase in crystallinity of Fe or Al oxides in either of the sediment types. A plausible explanation for this is that organic coatings formed upon drying may have 'protected' the oxides from aging. In the field of soil science it has been demonstrated that organic matter has an inhibitory effect on the crystallization of amorphous ferric hydroxides and that it keeps Fe in the amorphous and relatively reducible form (Drever & Stillings, 1997; Raulund-Rasmussen, Borggaard, Hansen, & Olsson, 1998; Schwertmann, 1966). Stumm and Morgan (1996) propose that adsorption or complexation of organic matter onto reactive sites on the iron hydroxides prevents nucleation and the formation of crystals by 'blocking' these sites. De Groot & Fabre (1993) elucidated that when pyrite oxidises (which would have occurred during the drying process), pyrite-Fe is transformed to amorphous Fe (oxy)hydroxides (which in turn are very effective at adsorbing P); however because the $Fe_{0.25M\ NH_2.OH.HCl}$ phase in this study was so small this may not be evident in the data.

6.4.4 Potassium chlorate extracts

This constituted the most important Fe and S phases in both sediment types. However, because this phase represents pyrite and monosulfides, as well as metals bound to organic S, it is difficult to ascertain the impact of drying on these individual components. Perhaps insertion of a NaOH leach before the $KClO_3$ leach, in order to remove this additional phase of organic matter would make the $KClO_3$ leach more specific to inorganic sulfides. Nevertheless, all reduced S-containing substances (organic or inorganic) have the potential to oxidise when exposed to oxygen and water (Giblin & Wieder, 1992), and consequently to cause acidification. Oxidation during the drying process can be expected to decrease Fe_{KClO_3} and S_{KClO_3} , and increase these elements in a similar magnitude in either one or more of the NaOAc, 0.25M- or 1M NH_2.OH.HCl pools. Even though in the peat, drying slightly reduced this pool (although by ~30% in Site 6), it did not increase these elements appreciably in any of the other geochemical pools. Rather, the shortfall, particularly in the Site 6 peat, seems to have mainly been transformed into a more recalcitrant (i.e. non-extractable) phase (see Tables 1 and 6 in Appendix 6.1). This is probably more related to the effect of drying on the organic complexes in this low pH sediment, than oxidation. It would appear then that dehydration *per se* will not bring about acidification (which supports the concept that water is required for acidification to occur; Singer & Stumm, 1970). The reason the sediments did not oxidise to any appreciable degree during the drying, is probably that they went more or less straight from an anaerobic state into the drying oven (where they were dried at 35°C for 12 days, see Chapter 3).

The fact that the floc responded differently to drying (as occurred in the pyro-P extracts) again points to differences in the types of organic matter in the two sediments, resulting in different binding mechanisms. In the floc of both sites Fe and S increased by ~21% in this leach as a result of drying. What might have caused this increase is difficult to ascertain. It might be implied though, that if the pool of potentially oxidisable S increases as a result of drying, the potential for acidification for the dried incubations would be greater (Chapter 4). However the contrary was the case (see below). The magnitude of $KClO_3$- and particularly of Cr-reducible S in the floc is in itself interesting. The major inorganic constituents of colloids in oxic freshwaters are generally alumino-silicates, silica and iron oxyhydroxide particles (Wilkinson & Reinhardt, 2005). The high $KClO_3$ (and Cr-reducible S) extractable Fe and S content of the Goollelal floc reflects the organic-rich and anaerobic environment in which the flocs

have formed, as well as presumably the high Fe content of the inflowing groundwater. Another apparent difference between the two sediment types is the speciation of Mn, the results suggesting the presence of MnS in the floc (this being the dominant Mn phase), but probably not to any significant degree in the peat (where Mn_{NaOAc} was the dominant phase).

6.4.5 Comparison of totals extracted by the scheme and total sediment concentrations

In terms of total extractable elements from wet and dried samples two main findings are apparent. Firstly, the scheme extracted less Fe, Al, S and Si from the dried than from the wet peat (e.g. in the case of Fe in the Site 6 peat, 27% less was extracted from the dry than from the wet samples, which equals the amount of Fe_{KClO_3} 'lost' from the dried when compared to the wet peat). In fact for the majority of the leaches, less of these elements could be extracted from the dried than from the wet peat (Ca and Mn being the only exceptions). So where did these elements go? It is possible that drying may have transformed a proportion of these elements into a more resistant form, not extractable even by *aqua regia*. Or alternatively, the organic coatings formed upon drying could not be efficiently removed with pyro-P (as discussed in 6.4.2). This has implications for sequential elemental extractions, as well as for *aqua regia* digests carried out for total metals in similar peat samples, when the commonly used pre-treatment of drying is used (e.g. Fe content could be underestimated). In terms of biogeochemistry, however, it was shown in Chapter 4 that the mean amount of Fe released under anaerobic conditions after 49 days of incubation was the same for both wet and dried treatments, suggesting that the organic coatings do re-dissolve under 'natural' inundated conditions.

Secondly, although organic coatings probably also formed on the dried floc particles (judging from the NaOAc extracts, and also the water repellence tests in Chapter 3), this sediment type, overall, and particularly the organic fractions, responded differently to drying than did the peat. The scheme, overall (with the exception of Si where less was extracted from the dried samples, and Ca where there was no difference between wet and dried samples), extracted more elements from the dried, than from the wet floc samples. Again, this may be related to differences in the nature of the organic matter. Floc structure (see discussion in Chapter 5) may also be partly responsible for the difficulty of chemically extracting elements from the wet floc. It is also possible that the very high P content (as well as the different P speciation between the peat and floc –

see Chapter 5) in the floc may have influenced the floc behaviour. Oxoanions such as PO_4^{3-} are well known to influence dissolution and crystal growth, as well as being able to reverse the surface charge of colloids (Stumm and Morgan, 1996). However the role of such anions in relation to sediment desiccation is unknown. It may be that upon drying, phosphates compete with organic matter for adsorption sites.

In total, recovery rates of most elements when compared to total sediment concentration, ranged between ~82 % (S in the dried peat and floc Site 3) and 120% (Ca in the dried peat Site 6). However, as discussed previously there were some significant differences in recovery rates between wet and dried treatments, and between sediment types, and thus, important consideration should always be given to sediment characteristics and the appropriate method of pre-treatment. The floc results demonstrate that simply deciding not to dry samples prior to chemical analysis may not necessarily yield the best results.

6.4.6 Relationship of drying-effects and acidification potential

This was discussed in some detail in Chapter 4, however, examining the specific responses of the two sites investigated in this chapter throws further light on these relationships. As mentioned in the introduction, decreases in pH are buffered by dissolution of $CaCO_3$ (equation 5.5), and the efficiency of this buffering effect depends on the amount of protons (i.e. acid) released and the amount of bicarbonate (and consequently hydroxide) ions that can be produced. Based on equations 6.1-6.3, 1 mole of FeS_2 produces 4 moles of H^+, and based on equations 6.5 and 6.6, 1 mole of $CaCO_3$ can neutralise 1 mole of H^+. Therefore in this case, 4 moles of $CaCO_3$ are required to neutralise the acidity produced by 1 mole of FeS_2, or a ratio of (say, Cr-reducible-) S to Ca of 1:2. This is obviously conservative because it does not take into account equation 6.4, nor the fact that probably all of the S_{KClO_3} is potentially oxidisable, but this is somewhat off-set by the fact that not all of the Cr-reducible S is FeS_2 (some of it will be FeS), and not taking into account other carbonates, such as Mg, etc. The molar ratio of Cr-reducible S to Ca (the majority of which is present as $CaCO_3$ as fractionation indicates) in the Site 3 peat is 1:1.68, in the Site 3 floc 1:1.36, in the Site 6 peat 1:0.66 and in the Site 6 floc 1:0.23.

Based on these very simplified and conservative calculations one would predict that inundation of all of these sediment samples under aerated conditions would bring about acidification, in the case of the Site 6 floc, severe acidification. Figure 6.4.1 (taken from Chapter 4 data) shows that in the peat the pH did indeed decline over time

(corresponding to increases in SO_4^{2-} and Ca - see Figures 6.4.2 and 6.4.3), whereas in the floc this only occurred in the Site 6 wet treatment (where it declined drastically from Day 21 onwards). The curbing effect of drying against pH decline is clear in the two graphs, however the fact that pH still declines over time suggests that the organic coatings formed upon drying do re-dissolve. This is in agreement with the literature on non-wetting soils where water repellence was found to be a transient soil property (although precise processes involved in these transitions are still poorly understood; Doerr, Dekker, Ritsema, Shakesby, & Bryant, 2002). The protective role of drying, however, cannot be attributed solely to the organic coatings, as was discussed in Chapter 4. As can be seen in Figure 6.4.1 (b), in the floc drying actually brought about an increase in pH, despite the unfavourable S:Ca ratios. Due to the magnitude of the increase in pH, this was speculatively (since nitrogen species were not measured) interpreted as being due to ammonification resulting from the release of large amounts of organic nitrogen (see Chapter 4). Furthermore, factors such as redox environment, potential buffering by organic anions and biological activity (mostly a reflection of nutrient concentrations) can have a dominating influence on sediment response. Therefore comparing the proportions of sediment S

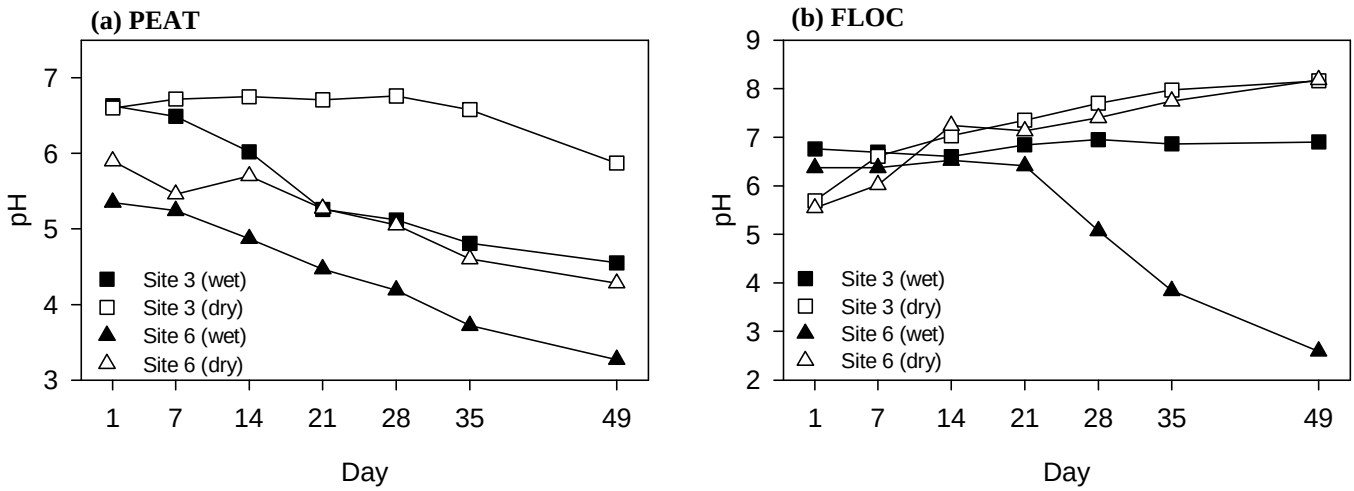


Figure 6.4.1: pH over time in aerated incubations of wet and dried (a) peat and (b) floc sediment.

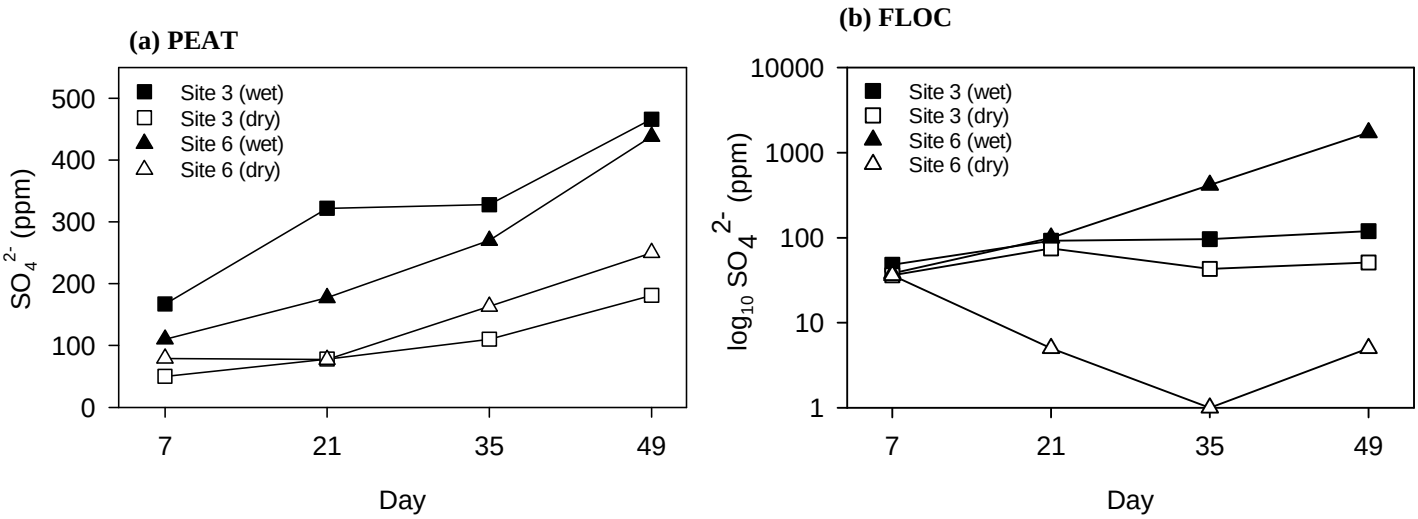


Figure 6.4.2: Sulfate concentration over time in aerated incubations of wet and dried (a) peat and (b) floc (please note log scale on y-axis) sediment.

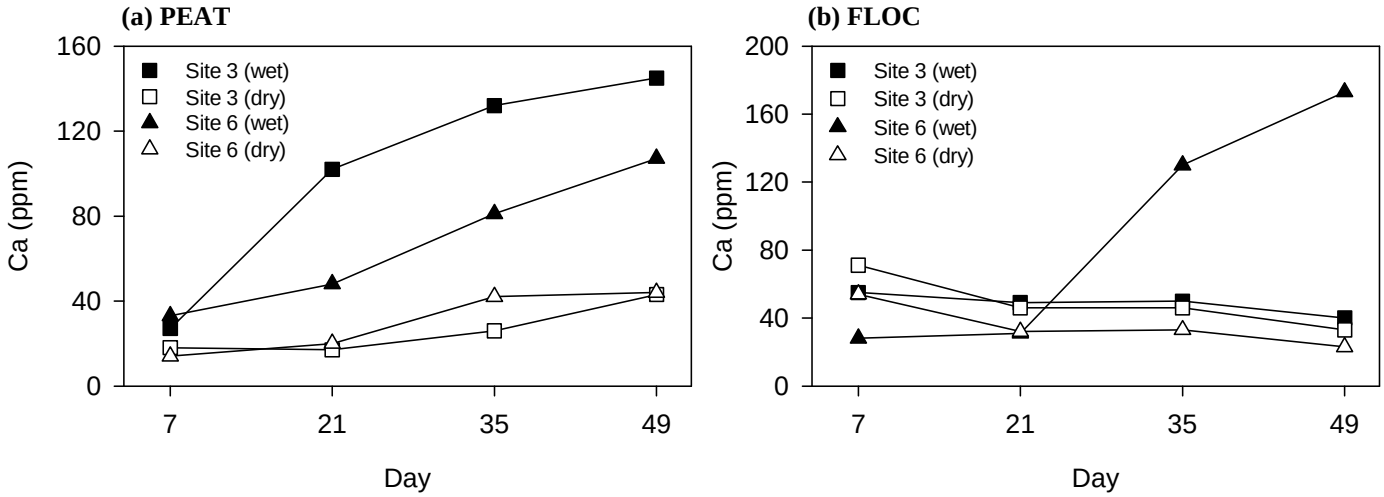


Figure 6.4.3: Calcium concentration over time in aerated incubations of wet and dried (a) peat and (b) floc sediment.

and base cation concentrations alone may not give an accurate enough indication of the potential for drought-induced acidification in such sediments.

6.5 Summary and conclusions

Sequential extraction of aquatic peat and floc sediments from two locations at Lake Goollelal revealed that the dominant Fe and S phases (representing between 70% to 90% of total sediment Fe and S) were potassium chlorate ($KClO_3$)-extractable (i.e. bound to organics and sulfides), and approximately half of this amount was chromium-reducible (i.e. pyrite, monosulfides, acid volatile and elemental sulfur). The 'free' amorphous Fe pool (0.25 M hydroxylamine extracts) in both sediment types was very small, and the crystalline Fe pool (1 M hydroxylamine extracts) virtually non-existent (even after drying). The dominant Ca pool was sodium acetate (NaOAc)-extractable (most likely calcium carbonate). This pool represents only a fraction of that required to neutralise the acidity which could potentially be produced by the S_{KClO_3} pool.

The fact less Fe could be extracted with NaOAc from the dried than from the wet sediments of both types was interpreted as being evidence for the presence of organic coatings in the dried sediments. The sodium pyro-phosphate extracts (which should remove these coatings) however were inconclusive. The reasons for this was that this reagent leaches not only adsorbed (e.g. coatings) but also metals organically bound by other mechanisms, such as complexation and chelation. Unlike Fe, more Ca (between ~ 8% - 25%) could be extracted with NaOAc from the dried sediments of both types, suggesting the absence of organic coatings on the $CaCO_3$ particles.

The main differences between the two sediment types were (1) the Fe and Al pyro-P pool was smaller in the floc than in the peat, reflecting the higher degree of humification of the peat; (2) the $KClO_3$-extractable Fe and S pools were larger (in the case of Site 6, quite significantly so) in the floc than in the peat, possibly reflecting the more labile nature of the floc organic matter (which promotes pyrite formation). Apart from the NaOAc-extractable pools, the PCA analyses suggest that the overall response to drying differed between the two sediment types. This was most obvious in the $KClO_3$ pool (Fe and S), where drying decreased this pool in the peat, but increased it in the floc. Furthermore, the scheme overall extracted less of most elements from the dried than from the wet peat, but more from the dried than from the wet floc. The most likely explanation for these differences are again most likely to be due to differences in the

characteristics of the organic matter, but probably also differences in nutrient status (the floc having very high total P and total N content compared to the peat; Chapter 3). The differences between the two sediment types revealed by sequential extraction were also reflected in the incubation results of Chapter 4. Incubation of the continuously wet peat under aerated conditions brought about a gradual pH decline in the peat of both sites, this having been predicted by the unfavourable S:Ca ratios. Drying 'dampened' this decline by a mean of ~1 pH unit over the 49 day incubation period. This dampening effect was attributed to the presence of organic coatings on the dried sediments. In the floc however, with the exception of the Site 6 floc which had extremely high oxidisable S content and extremely low Ca content, incubation under aerated conditions did not bring about a decline in pH, and in the dried floc the pH actually increased (Chapter 4). This demonstrated that biogeochemical processes (related to inherent sediment characteristics) can have an overriding influence on how a sediment will respond to drying and oxidation, regardless of 'unfavourable' sediment S to Ca ratios. Specifically, high nutrient concentrations and the reactivity of organic matter appear to be able to biogeochemically buffer against acidification (even though this may not necessarily be a desirable outcome either, see Chapter 5).

The main conclusion of this study is that drying *per se* will not bring about acidification, since drying did not appreciably reduce the oxidisable Fe and S pools in either sediment type (and in the Site 6 peat the majority of Fe and S 'lost' from this pool appears to have moved into the non-extractable pool, rather than the more reactive pools). The main impacts of drying in the sediments investigated were an increase in Ca_{NaOAc} (i.e. adsorbed/exchangeable/carbonate), and a decrease in Fe_{NaOAc} (the latter of these phenomena being most likely due to organic coatings formed upon drying). It can be assumed (although this has not been investigated to date) that the other organic-rich wetlands on the well-buffered Spearwood dunes have similar high levels of oxidisable S as Lake Goollelal, since they formed under similar circumstances. Not all of them have a nutrient-rich organic floc layer which would potentially buffer against drought-induced acidification. Where the peat layer is deep, the underlying limestone lithology is essentially isolated from the surface layers, and would therefore not be available for buffering. The considerable amounts of acidity likely to be produced, not by drying but by oxidation of the sediments due to aeration and low water levels, would very likely override the buffering potential provided by the alkaline groundwater feeding these wetlands.

CHAPTER 7
SYNTHESIS: MANAGEMENT OF GROUNDWATER-DEPENDENT WETLANDS IN DRYING ENVIRONMENTS – THE ROLE OF WETLAND SEDIMENTS

7.1 Introduction

The motivation for this study was in no small part driven by an obvious need for water resource agencies to adopt a more proactive approach to wetland management, particularly in view of projected climate trends. In the past decade, increasing instances of eutrophication and acidification of wetlands on the Swan Coastal Plain (SCP), and particularly on the Gnangara groundwater mound (GGM), have coincided with gradually decreasing ground- and surface water levels. In most instances, these problems came as a 'surprise' (sensu Gunderson, 1999) to management agencies, i.e. they were not anticipated, and the link between water drawdown and water quality issues has only very recently been acknowledged. The SCP supports a number of groundwater dependent ecosystems (GDEs), and the majority of its wetlands are groundwater flow-through systems (Townley et al., 1993). There is often an interdependency between these wetlands and the underlying aquifer. For example, many of the wetlands act as either groundwater recharge or discharge lakes on a seasonal basis (Townley et al., 1993). It is because of this interdependency, that integrated management of water resources (both surface- and groundwater) and wetlands is not only warranted, but essential to ensure the sustainability of the ecosystem and the water it provides (see Anon., 2005).

Water allocation issues have become the principal business of wetland management agencies in Perth. It is postulated that the cause of the groundwater drawdown is primarily a drying climate onto which (over-) abstraction is superimposed (Vogwill, 2004; Yesertener, 2003). To put this into perspective, however, (winter) rainfall between 1976 and 2001 was ~10% lower than between 1925-1975 (IOCI, 2002), while public water consumption between 1976 and 2001 alone increased by ~300% (see Figure 1.4 and 1.5, Chapter 1). Reduced rainfall and increased consumption create unfortunate positive feedback loops. Reduced rainfall causes reduced aquifer recharge on the one hand, while at the same time causing an increase in aquifer

withdrawal (due to increased demand for water in times of drought). In spite of higher rainfall since 2001, water levels in the mound continue to decline (Vogwill, 2004). This has been attributed to aquifer depletion (Vogwill, 2004). The aquifers (both the superficial, and the underlying confined aquifers which have also suffered declines; see Figure 1.2, Chapter 1) must first be replenished before they can service groundwater dependent ecosystems such as wetlands. In fact, the Gnangara mound has been depleted to the extent that hydrological modelling suggests that even if all abstraction were to cease, the groundwater table would continue to decline (given projected climate trends; Vogwill 2004).

Water level management of wetlands on the GGM has become a major challenge to resource management agencies. Where regulation of public water supply and private abstraction has failed to achieve the stipulated minimum water level criteria, it has been deemed necessary, in some cases, to artificially supplement affected wetlands with groundwater in order to maintain 'environmental values' associated with these wetlands (Department of Environment, 2004). Due to limited resources (both financial and actual water) management agencies are faced with the dilemma of having to prioritise. Which wetlands have ecological and/or social values 'worthy' of artificial supplementation, which ones are better 'written off' (i.e. left to dry)[*]? How will the infill water affect the water quality of the wetland? How much and when should pumping take place? To date desirable or optimal pumping strategies for the GGM wetlands do not exist, mainly due to the lack of a model which properly handles lakes which experience significant seasonal fluctuations (Townley et al., 1993). Moreover, artificial supplementation cannot be regarded as a permanent solution. These are indeed difficult questions, and what should they be based on? Water level management on the GGM has traditionally used littoral vegetation, aquatic macrophytes and macroinvertebrates as the basis for determining Ecological Water Requirements (EWRs), and the primary indicators for monitoring change (Water Authority of W.A., 1995). The problem with 'monitoring change' is that when a change is detected, it may already be too late to prevent adverse environmental impacts. As a consequence reactive mitigating measures (such as artificial supplementation of water levels) must be taken, and one is always one step behind a potential 'surprise', or even crisis. In the case of species extinctions due to acidification, for example, it is obvious that it was not the

[*] This has occurred, e.g., in the case of Coogee Springs (Benier & Horwitz, 2002), where infill water simply 'disappeared' through the bottom sediments. Another example is Lake Gnangara (see Figure 1.6, Chapter 1) which is considered to be 'too far gone' to be worthy of supplementation. These cases are classic examples of systems whose natural resilience has reached their limits and have

breech of the set water level criteria that caused the local extinctions (see e.g. Sommer & Horwitz, 2001), but the acidification. Likewise, the proliferation of Chironomid midges following drought and reinundation would not have been caused by the low water table itself, but by the increased amount of nutrients in the water column. Such 'surprises' (or 'unexpected ecosystem behaviour') are not surprising (even though in hindsight they certainly should have been); they appear to be the rule rather than the exception in co-evolving systems of humans and nature (Gunderson, 1999). They are a component of what in ecological theory is called the 'adaptive cycle'. The adaptive cycle describes complex social-ecological systems in which change is triggered by surprises (Janssen, 2004). Clearly, the 'change' that must occur in this case is that the source of acidification, eutrophication and other biogeochemical manifestations must be taken into consideration when setting EWRs and water level criteria. The objective of change (a policy change in this case) is to prevent a loss of natural resilience which could shift a system from one ecological state to another (usually a less desirable one) (Scheffer et al., 2001).

The notion of 'ecological resilience' is based on the assumption that ecological systems operate at or near a global equilibrium, whereby resilience is the ability to return to an equilibrium following a perturbation (see discussion in Gunderson, 1999). It is comparable to what in chemistry is termed the 'buffering capacity'. pH buffering capacity, for example, is the ability of a solution to resist a change in pH when acids or bases are added. Phosphorus buffer capacity is the ability of a soil or sediment to adsorb or release phosphorus resulting in a more or less steady concentration of phosphorus in solution. An alternative definition of resilience, one that probably better reflects the dynamic complexity of natural systems, emphasizes conditions with more than one equilibrium, '…where instabilities can flip a system into another regime of behaviour, i.e., to another stability domain' (Holling, 1973). Resilience then is measured as the magnitude of disturbance that can be absorbed before the system redefines its structure by changing the variables and processes that control behaviour (Gunderson, 1999). Therefore, the response of a wetland to disturbances such as drought, for example, is determined by its resilience, its resilience in turn being a direct reflection of overall wetland function. For resilience management to be effective the variables that determine or control the resilience of a natural system must be identified and understood. The aim

consequently reverted to a different ecological condition (Scheffer, Carpenter, Foley, Folke, & Walker, 2001), from which it will be difficult (if at all possible) to recover.

of this chapter is to discuss how a biogeochemical analysis of critical sediment types can characterize wetland function and response (i.e. resilience) to hydrological change.

7.2 The role of wetland sediments in ecosystem resilience management: the example of Lake Goollelal

The wetlands on the GGM support most of the known types of wetland sediments found elsewhere on the planet. These range from different sized particles of quartz grains and other mineral components to biogenic materials such as marl, peat, diatomite and various organic 'oozes' (Semeniuk & Semeniuk, 2004). Often an individual wetland will support a combination of a number of these sediment types. There is also considerable variation in the types and amounts of important elements (e.g. carbon, iron, phosphorus, nitrogen, etc.) present in the different wetland sediments (see Davis et al., 1993). Because of this spatial heterogeneity it is to be expected that each individual wetland within a watershed, although linked by the same aquifer, will respond somewhat differently to water level drawdown and drying. Hence, although it generally makes sense to manage wetlands from a watershed perspective, certain management objectives can only be met if wetlands are managed individually. Moreover, as the following discussion of the Lake Goollelal sediments will show, the 'patchiness' of sediment characteristics (both in a horizontal and vertical sense) extends to within individual wetlands. Therefore, for management policies to be successful, they must be linked to appropriate spatial (and of course also temporal) scales (Holling & Gunderson, 2002).

7.2.1 Summary of the biogeochemical characteristics of the Lake Goollelal sediments

In this thesis the issue of within-wetland spatial heterogeneity was dealt with by locating a number of sampling sites in different geographic sections of the lake (see Chapter 3), and by treating any characteristically different sediment types separately. The organic component of the sediments of Lake Goollelal comprises two distinct layers: suspended detrital floc and underlying peat. Given the depth of this organic component (in particular the peat), the underlying (and surrounding) mineral component may safely be disregarded in terms of response to drying and rewetting. The two organic compartments were found to consist of between 67% and 82% organic matter, and were rich in iron and sulfur (a reflection of the marine influence during peat formation). As such, the potential for drought-induced acidification must inevitably be considered. Nitrogen to organic carbon ($N:C_{org.}$) ratios indicate that the floc is probably

largely of aquatic (algal) origin, in contrast to the peat which appears to be chiefly of vascular plant origin (possibly aquatic macrophytes and the remains of terrestrial plants and trees such as *Melaleuca* spp.). As such it could be expected that the floc organic matter would be more reactive than that of the peat. This high reactivity of the floc organic matter was reflected in the very high concentration of nutrients (P & N), metals, microelements and also of oxidisable sulfur. However incubated continuously wet floc (1:50 sediment to water ratio) released very little P, and pH was virtually identical, in both anaerobic and aerated treatments. This suggests that the floc, although obviously very reactive in terms of nutrient (and other elemental) scavenging, must be relatively inert in the hydrated state, regardless of dissolved oxygen concentration. This characteristic was hypothesized to be due to the particular physical structure of the floc. Continuously wet incubated peat was also relatively 'inert' under anaerobic conditions, although a much greater proportion of total sediment P was released from the peat than from the floc (~6.5% of total sediment P from the peat by Day 49 of the incubation, compared to only ~0.10% in the floc). In contrast to the floc, aeration of the continuously wet peat resulted in less P being released, as well as acidification (pH 4.7 on Day 49 of the incubation of the aerated slurries, compared to 6.6 in the anaerobic slurries).

One of the more interesting findings of this research was the drying-induced water repellence of both sediment types, and the effect that this had on the biogeochemical cycling of elements upon re-inundation. Although not surprising in hindsight, water repellence is not something that is usually associated with aquatic sediments. This water repellence, known from the soils sciences to be caused by the formation of organic coatings on sediment particles, had significant consequences, both for the retardation of acidification and the exacerbation of eutrophication. Organic coatings consist of non-polar (i.e. hydrophobic) aliphatic hydrocarbons as well as polar (essentially hydrophilic) molecules originating from organic sources ranging from bacteria, fungi and algae to higher plants (Doerr et al., 2000). How exactly these compounds are bonded to soil particles remains unclear (Dorr et al., 2000). In the peat incubations, drying 'dampened' the oxidative effects caused by aeration in that significantly less sulfate was released and pH also declined less. In the floc sediment, drying very significantly increased total filterable phosphorus (TFP) concentration under both anaerobic and aerated conditions. Alongside the considerable release of TFP in the dried/rewet floc anaerobic slurries, pH decreased, and iron and calcium concentrations increased markedly upon rewetting, and recovered only slowly over

time. On Day 49 the pH of the dried and aerated floc slurries was comparatively high (mean 8.1) and, in view of the high total nitrogen concentration of the floc, it was inferred from the literature that this was probably largely the result of ammonification, spurred on by drying-induced release of organic nitrogen.

Sequential elemental extractions revealed that the great majority of phosphorus in both sediment types was organically bound. In the peat, drying decreased the potentially mobilisable P fractions in favour of P_{NaOH} ('bound to Al-humic complexes; polyphosphate'; Ruttenberg, 1992). This was interpreted as being due to increased P sorption capacity of the sediment. In contrast to the peat, drying substantially increased easily mobilisable P (P_{MgCl_2}), and in this case, this was attributed to the very high amount of drying-induced mineralised P compared to Fe (and Al) content of the floc (to which this P could potentially bind). Comparison of the fractionation results with the incubation study showed that an apparent drying-induced increase in sediment affinity for P does not necessarily equate to less P being released upon re-inundation. Furthermore, significantly less P was released from the continuously wet peat in the anaerobic slurries than potentially mobilisable based on P fractionation. On the other hand, more P was released anaerobically from the dried floc than potentially mobilisable, suggesting possible release from the NaOH and/or ashing/HCl P pools (considered to be largely unreactive organic P).

The dominant iron and sulfur phases in both sediment types were potassium chlorate ($KClO_3$)-extractable (i.e. bound to organics and sulfides), and approximately half of this amount was chromium-reducible (i.e. pyrite, monosulfides, acid volatile and elemental sulfur). The 'free' amorphous iron pool (0.25 M hydroxylamine extracts) in both sediment types was very small, and the crystalline iron pool (1 M hydroxylamine extracts) virtually non-existent (even after drying). This indicates low P buffer capacity, unless much of the reduced Fe were to oxidise to Fe-hydroxides to which P could bind. The dominant calcium pool was sodium acetate (NaOAc)-extractable (most likely calcium carbonate). This pool represented only a fraction of that required to neutralise the acidity which could potentially be produced by the S_{KClO_3} pool. Drying did not markedly impact the size of the S_{KClO_3} and Fe_{KClO_3} pools (and conversely the potential for acidification). The main reason for this was presumably the speed at which the sediments were dried (i.e. there was not enough time for significant oxidation to take place before dehydration). Comparison with the incubations suggests that protection from acidification in the dried floc was provided by the intense microbial activity

resulting from drying (specifically ammonification) which buffered against a decline in pH. This nicely demonstrated that chemical buffering capacity (e.g. the amount of acids added to a system versus the amount of base available for neutralisation) and biogeochemical buffering capacity are not the same thing. It could be argued that which-ever can override the other in response to disturbances would determine the resilience of the system.

7.2.2 Possible response scenarios

These sediment characteristics (see Chapters 3, 4, 5 and 6 for details) allow a number of plausible responses to be envisioned, should water levels fall. In line with the theory of adaptive cycles, resilience management (i.e. a management approach based on resilience) does not require a precise capacity to predict responses but only a qualitative capacity to maintain systems that can absorb and accommodate future unexpected events (Holling, 1973). Three water level scenarios are discussed below.

Scenario 1: Water level falls to surface of floc layer (then refills)

Although a number of GGM wetlands contain suspended detrital floc (colloquially referred to as 'false bottom' and sometimes as 'metaphyton'), this sediment type has not previously been characterized for the SCP. The work presented in this thesis suggests that suspended detrital floc plays a very important, if not dominant, role not only in the biogeochemical cycling of elements, but possibly also in the physical characteristics of the water body (discussed in Chapter 3). In terms of declining water level, the floc also has an important function because it is the first part, and often the only part, of the wetland's sediments to become aerated and subsequently dry. The scenario being discussed here corresponds to phase 2 in the general model (which does not show a floc component) presented in Chapter 2 (Figure 2.6.1). As suggested in the model, this is generally an undesirable situation for the wetland to be in for any length of time. Concentration of nutrients in the surface- and porewater and increased solar irradiation will likely cause algal blooms, exacerbating anaerobic conditions below (by increasing oxygen demand of decaying algal biomass). However, the incubation experiments (Chapter 4) imply that the increase in nutrient concentration (specifically phosphorus) will probably be solely from evapo-concentration and not from additional anaerobic release from the floc itself. Moreover, although not tested in this study, it likely that at least some of the increase in phosphorus concentration would be sequestered by the floc. An unpublished study carried out on Lake Joondalup (see

Figure 1.1, Chapter 1, for location) 'metaphyton' (essentially a type of suspended calcareous detrital floc) showed that additions of phosphate up to 500 μg L^{-1} were efficiently taken up by the 'metaphyton', even in the absence of light (Wong, 2003). Once taken up by the floc, the phosphorus is unlikely to be released again, as long as the floc does not dry. In this respect then, reduction of the water level roughly to the surface of the floc might have a positive effect in lowering nutrient concentrations once the lake has refilled. This point has implications for artificial water level maintenance of eutrophic wetlands. For instance, much water could be saved, while at the same time improving water quality, if the summer water level were allowed to drop to the surface of the floc layer, rather than maintaining higher water levels.

Midge plagues during the low water stage (assuming water temperature does not exceed the tolerances of the midges) however could be an outcome. Concentration of nutrients, as well as of the floc, a suspected food of midge larvae (see for instance Iovino & Bradley, 1969; Wetzel, 2001), would spur this on. Aeration of some or all of the floc layer, e.g. in the event of strong winds, would be unlikely to have any significant effects, based on the incubation studies. The relatively small release of sulfate would probably quickly be taken up by algae and microbes. In this scenario sediment bulk characteristics alone (e.g. high P and N concentrations, certain elemental ratios, etc. – see Chapter 3) would not be sufficient information for predicting response. This is because the apparent physical characteristics of the floc appear to play an overriding role in determining floc behaviour. It is quite possible that all types of organic detrital floc found in SCP wetlands behave in this manner (i.e. remain relatively inert regardless of oxygen concentration, as long as their structure has not been destroyed by drying), however, this is something that requires confirmation through further experimental work.

Scenario outcome: Probably little or no decline in ecosystem resilience (as long as nutrient inputs are not increased). Possibility of midge plagues during low water phase which may incite complaints from residents. Good prospect of recovery once water levels have been restored, and potentially improved water quality after refilling due to nutrient uptake by floc during low water phase.

Scenario 2: Water level falls to surface of peat, floc dries (then refills)

This approximates phases 3 and 4 in the general model presented in Chapter 2 (Figure 2.6.1). Once the floc dries, it is likely to become permanently part of the

consolidated sediment (Childers et al., 2003). This has a number of significant consequences. For example, it will no longer be as effective as a sink for nutrients and other pollutants. Drying ruptures the floc structure, and the proportion of exchangeable/loosely sorbed P increases substantially at the cost of previously un-extractable (i.e. unavailable) P (Chapter 5). Humic anions efficiently compete with phosphate for sorption sites on the floc particles. The humic substances form coatings on the floc particles, rendering these severely water-repellent (Chapter 3). Upon re-inundation very unpleasant odours will be emitted. There will be a huge pulse of nutrients into the water column. This can be expected to spur on intense primary productivity (and associated problems such as algal blooms and midge swarms, see Chapter 2) and probably quickly reinstate anaerobic conditions in the hypolimnion. Decomposition of this material can be expected to result in the release of considerable amounts of CO_2 into the atmosphere. In spite of high pyrite content, and unfavourable S:(Ca + Mg) ratio (Chapter 3 and 6), acidification is unlikely for two reasons. Firstly, the organic coatings provide temporary protection from excessive oxidation, and secondly the quick re-instatement of anaerobic and eutrophic conditions would prevent this. The high productivity, reinstatement of anaerobic conditions, and adequate supply of iron and calcium from the infill water create a situation conducive to the (re-) formation of suspended detrital floc. However, it is not known how quickly these form. It may possibly require many decades to build up to the depths (~0.5 m) encountered at Lake Goollelal today[*].

The underlying peat would have been protected from oxidation if a 'crust' would have formed by the dry floc (compare Phase 3 in Figure 2.6.1). However, in this study the dry floc tended to crack in which case some oxygen would have penetrated the underlying peat. Because the peat in this scenario would still be completely wet, some acidification may occur. Upon reinundation however, the anaerobic and eutrophic conditions created by the floc (now of course part of the consolidated sediment) would quickly return the peat to its former reducing conditions.

Scenario outcome: Loss of the suspended floc would reduce the capacity of the wetland to cope with ongoing nutrient inputs: decline in resilience. Severe ongoing eutrophication can be expected until floc layer can be re-established. Potential time-frame for recovery unknown; 'surprises' likely.

[*] At Lake Joondalup though suspended detrital floc appears to quickly redevelop after seasonal draw down on an annual basis (pers. obs.). At this wetland though, there is no peat, and the mineral component of the sediment (including the floc) consists primarily of calcite.

Scenario 3: Water level falls below the surface of the peat, peat and floc dry (then refills)

This approximates phase 5 in the general model in Chapter 2. A very intense drought, or long-term drawdown of the water table would be required to create this scenario. This is because peat has a very strong water-holding capacity (Fuchsman, 1986). In addition to the consequences described in scenarios 1 and 2, the peat now also dries. This causes some irreversible changes in the peat (discussed in 2.2, Chapter 2), in particular the susceptibility to mineralization is increased, and the peat's water holding capacity is decreased, so that it will dry more rapidly in future drawdown events. Once irreversible physical changes have occurred the wetland becomes highly vulnerable to a shift to another ecological (stable?) state. In this scenario, the wetland sediments are very susceptible to fire (a growing problem on the GGM). Some peat fires on the GGM have burnt underground for months (e.g. Pipidinny Swamp, Coogee Springs, Lake Wilgarup, and most recently Lake Neerabup) creating a human health hazard (Hinwood et al., 2006), and environmental problems associated with acidic groundwater (Appleyard et al., 2004). This scenario would be quite rare in the history of organic-rich wetlands and would be considered a 'catastrophic event' because it is contra-indicative to the build-up and persistence of organic sediments (Horwitz et al., 2003; Horwitz et al., 1999).

Upon reinundation, the sediment (peat and ex-floc) will initially resist wetting due to the organic coatings formed and other physical changes in the peat. However, substantial amounts of phosphorus and nitrogen (primarily from the ex-floc), and much of the sediment calcium, will immediately be released into the water column (see Chapter 4). Thus, anaerobic conditions will probably be reinstated before the peat (and ex-floc) can further oxidise to any considerable degree. In the absence of a suspended floc layer, however, a peat such as the Lake Goollelal one, if allowed to oxidise and/or oxidise and dry, can be expected to result in acidification of the water column upon reinundation if the infill water does not contain enough buffering material to neutralise the acids formed. In the case of the dry sediments having been burnt, the loss of organic matter would decrease their ability to become reduced after re-inundation. Although organic coatings may provide some temporary protection, the sediments will be more likely to oxidise. The large amounts of iron released from the oxidation of pyrite (plus iron provided by the infill water) would remove much of the phosphorus in the water column, ultimately reducing the rate of organic matter additions to the sediments,

exacerbating the problem. Every subsequent drought-induced acidification event would further reduce the wetland's resilience.

Scenario outcome: High vulnerability to fire during the dry phase. If a fire has consumed large amounts of organic matter, acidification will be likely. In the absence of fire, eutrophication of the water column, and erosion of pH buffering leading to potential future acidification if the drying/wetting is repetitive in well-buffered systems. Permanent physical changes in sediment properties. Loss of resilience and probable change to a different ecological state.

Similar scenarios could be created for all of the wetlands susceptible to water level drawdown on the GGM, if a basic knowledge of their sediment characteristics is available. The point of having these here is to emphasise how very complex biogeochemical and physical relationships can be organised into information about possible transformations in a comprehensible way. Such scenario planning can then be used to facilitate discussion and initiate management actions in order to curb future 'surprises'.

7.3 Conclusions

Although the water levels of Lake Goollelal are at present stable, at least four similarly-sized (permanent) wetlands on the GGM with similar sediment characteristics (i.e. suspended organic floc overlying peat, although with differing elemental concentrations; see Davis et al., 1993) are experiencing rapidly declining water levels. It is more than likely that such wetlands exist elsewhere on the planet where drawdown or water inflow is a problem. Certainly there are such wetlands in similar geomorphic settings around the coast of southwestern Australia. Hence the suitability of Lake Goollelal as a case study for these investigations should be judged against this criterion. Because of the high organic content of the sediments (and also high concentration of crucial elements such as N, P, Fe and S) responses may have been more pronounced than might be expected in less 'rich' systems. As previously mentioned, every wetland has somewhat different bulk sediment characteristics, and hence should be assessed individually in terms of water level management. In terms of water level management, and particularly water level management with a focus on resilience, it can generally be concluded that regardless of whether a suspended detrital floc layer is present or not, it is generally not beneficial to let organic-rich wetland sediments dry. If they are nutrient rich, previously sequestered and immobile nutrients (not to mention other pollutants such as hydrocarbons, etc.) will be released into the water column and cause

eutrophication. If they are nutrient poor, and perhaps in the absence of a floc layer, drying, rewetting and oxidation will cause acidification of the water body (assuming they contain reduced sulfur, which most coastal peats do). In addition, it can be argued that there is a 'global citizen' obligation to keep aquatic organic sediments saturated for most of the year because these are significant carbon stores. Hence the role of their conservation also needs to be considered in terms of climate change mitigation strategies (Bergkamp & Orlando, 1999). Furthermore, organic sediments are a wonderful accumulated record of past environmental conditions and allowing this to disappear would deprive us of valuable knowledge which would certainly also improve our understanding of how these systems function today.

Answers to questions outlined in Chapter 1:

1. *Can simple sediment physical and bulk characteristics (including proxies such as elemental ratios), and with the help of univariate, bivariate and multivariate statistics, be used to infer within-wetland function, including responses to disturbances such as drought?*
   Yes, much can be learned by carrying out a few simple sediment analyses, and such analyses should always be the first step in devising management plans. However, inference to within-wetland function and responses to disturbances such as drought must be made cautiously because the biological (microbial) component of the sediment can override straight geochemical reactions (see below). Furthermore, in the case of detrital floc, not enough is known about the physical-biogeochemical interactions that occur in this organic entity.

2. *Will aeration of the sediments result in acidification if the buffering capacity is low?*
   In the peat, yes. In the floc, also yes, but only if aeration continues for a long period of time. Sulfide oxidation was very much slower in the floc than in the peat, and over the 49-day incubation period pH did not decline. The reason for this slow response is not known but may be related to the physical structure of the floc.

3. *Does drying exacerbate acidification under aerated conditions?*
   No, on the contrary. The sediments developed organic coatings during drying which gave them water-repellent characteristics similar to those described for terrestrial soils. These coatings appear to slow down the oxidation of reduced substances. The significance of this is that the water body will have more time to (re-)develop anaerobic conditions, and hence prevent acidification. In the floc, the drying-induced release of huge amount of nutrients and the greater availability of labile organic matter even resulted in a significant pH rise (interpreted as being due to ammonification). This demonstrated how biogeochemical reactions can override oxidation, even in the absence of sufficient amounts of neutralising compounds such as $CaCO_3$.

4. *Will drying/rewetting cause acidification if anaerobia is quickly restored?*
   In the peat, no. After an initial decline of 0.5 pH units, the pH of the dried and undried sediments was identical under anaerobic conditions. In the floc, temporarily yes. It took the dried/rewet floc

49 days to recover from an initial pH decline of 1.4 pH units. However, this was probably not due to the oxidation of FeS_2, but to the build-up of CO_2 resulting from increased microbial activity. Increased microbial activity in turn was brought about by drying-induced higher availability of labile organic matter and nutrients.

5. *Will aeration decrease the amount of phosphorus released from continuously wet sediments?*
In the peat, yes, and this was becoming more significant over time as aeration continued (and more reduced Fe was being oxidised). In the floc, no. Aeration did not appear to have an effect on the amount of phosphorus released. The reason for this is not known but may be related to the physical structure of the floc.

6. *Will more phosphorus be released from dried/rewet sediment under anaerobic conditions than from sediment kept continuously wet (and anaerobic)?*
For both sediment types, yes. However, in the peat only statistically insignificantly so, while a huge amount of phosphorus was released from the dried/rewet floc. This was because of the very high content of P in the floc compared to the peat (nearly seven times more), but also probably because of the low Fe:P ratio in the floc. A low Fe:P ratio (in non-calcareous sediments) indicates that there will not be enough Fe to bind the amount of P released.

7. *Will aeration decrease the amount of phosphorus released from dried/rewet sediments?*
Yes, but in the floc there was still significantly more P in the aerated dried/rewet than in the continuously wet floc. This aerobic release of P was again attributed to the low Fe:P ratio. In the peat roughly the same amount of P was released from both aerated treatments.

8. *How will drying affect the forms of phosphorus in these organic sediments?*
In the peat drying decreased the potentially mobilisable P fractions, probably due increased P binding capacity of the newly exposed mineral surfaces. At the same time the NaOH-extractable fraction (bound to humic complexes and polyphosphates and generally considered to be unreactive) increased markedly. In spite of this, more P was released (albeit insignificantly) from the dried/rewet than from the continuously wet incubated peat. Because less P was released than potentially mobilisable (from both treatments) it cannot be ascertained whether more P was released from the dried/rewet anaerobic peat because of stronger reducing conditions, or whether some of the NaOH fraction (e.g. polyphosphates) was released, or both.
In the floc drying greatly increased the exchangeable/loosely sorbed P fraction, however this could not convincingly be attributed to a decrease in sediment P affinity because less P could be extracted from the other easily mobilisable fractions ($NaHCO_3$ and CDB). Furthermore, when P was added to the dried floc (after having removed adsorbed/loosely bound P) it also retained considerably more P than the wet floc did (indicating an increase in sediment P affinity). It is postulated that the most likely reason for the increase in adsorbed/loosely bound P was the very high amount of drying-induced mineralised P compared to Fe (and Al) content of the floc.

9. *How will drying affect the elemental partitioning in these organic sediments?*

The main impacts of drying on elemental partitioning were an increase in adsorbed/ exchangeable/carbonate calcium (Ca_{NaOAc}), and a decrease in Fe_{NaOAc} in both sediment types (the latter of these phenomena being most likely due to organic coatings formed upon drying).

10. *If an acidification response is observed in the incubation study in Chapter 4, will this be due to drying-induced changes in iron and/or sulfur partitioning, or exclusively due to oxidation?.* Drying *per se* is unlikely to bring about acidification because drying did not appreciably reduce the oxidisable iron and sulfur pools in either sediment type. In the more acidic of the two peat samples investigated, these pools were reduced by ~7% but this did not show up in any of the other pools (i.e. the 7% became non-extractable).

An emerging pattern in the answers to the above questions is that the floc often responded contrary to expectations. Were such sediments to dry there would surely have been a few 'surprises'. What both the scenarios and the answers to above questions suggest is that the resilience of Lake Goollelal in fact lies in the floc. The floc dominates the ecological functioning of the wetland and characterises it in its present state. Therefore resilience management of similar wetlands should focus on maintaining this floc, and the way this can be achieved is to keep it permanently hydrated. Although this study has revealed much interesting information about the nature of organic aquatic sediments and their resilience, there were inevitably a number of limitations. The main one was probably that a combined peat-floc sediment sample was not also taken through the incubation experiment. This would have provided results better representative of what might happen in the field. Inclusion of nitrogen cycling as a variable would have been useful in interpreting the incubation results. In the elemental fractionation studies having a third site would have certainly made interpretation of results easier and also enabled more rigorous statistical analyses to be used. Micrographical analyses may have provided some insight into the physical structure of dried and undried sediments (especially in relation to organic coatings and the physical structure of the floc in dried vs. wet sediment). Unfortunately these things could not be done due to time and financial constraints. As is commonplace in science, the more one discovers, the more one realizes how little one knows. Accordingly, a number of questions and future research directions have arisen from this study:

1. What is the nature of physical-biogeochemical interactions in the suspended detrital floc? How can this be used to improve management/conservation of wetlands that support this sediment type? How long does it take for the suspended detrital floc to become incorporated into the consolidated sediment in the absence of drying? What different types of suspended detrital floc occur in SCP wetlands, and do they all act similarly to the Lake Goollelal one?

2. What are the factors that cause chemical buffering responses (or lack thereof) to be overriden by biogeochemical processes in organic sediments? Nutrient status and lability of the organic matter are certainly factors, as this work has shown, but how resilient are the biogeochemical buffering processes? What does it take for them to be 'out-stripped'?

3. What is the significance of Fe:P ratio in organic pyritic aquatic sediments? So far this has only been investigated for non-pyritic sediments.

4. How does drying affect different types and forms of organic matter? How are organic coatings formed? How do these affect the micro-biota of wetlands?

5. How can an understanding of the nature of suspended detrital floc be used to manage nuisance chironomid plagues? Do the midges consume the floc? Is it the detrital organic matter they are after, or the microbial community that lives therein? Why is drying of detrital floc often associated with nuisance chironomid plagues?

Aquatic sediments, especially organic ones, play a crucial role in the ecological functioning of wetlands and their resilience to withstand disturbances such as drought. Unfortunately whilst policies appear to be working there is little or no incentive for learning. This study has shown that much can be learnt from studying ecological systems before they are confronted with a major disturbance. This should ideally be the focus of wetland management on the SCP, especially in view of the projected drying climate trend.

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APPENDICES

Chapter 3

3.1 Lake Goollelal hydrograph

3.2 Independent samples testing for differences in sediment characteristics between Lake Goollelal peat and floc sediments.

3.3 Tests of Normality of elemental distribution within Lake Goollelal for peat and floc sediment.

3.4 Comparison of Lake Goollelal sediment total elemental composition by XRF, Aqua Regia/ICP-AES, Total S Analyser, sequential extraction schemes (Hall et al., 1996 and Ruttenberg, 1992), and Davis et al. (1993).

3.5 Some elemental concentrations (mg L^{-1}) of water drained from Lake Goollelal floc taken from six locations around the lake.

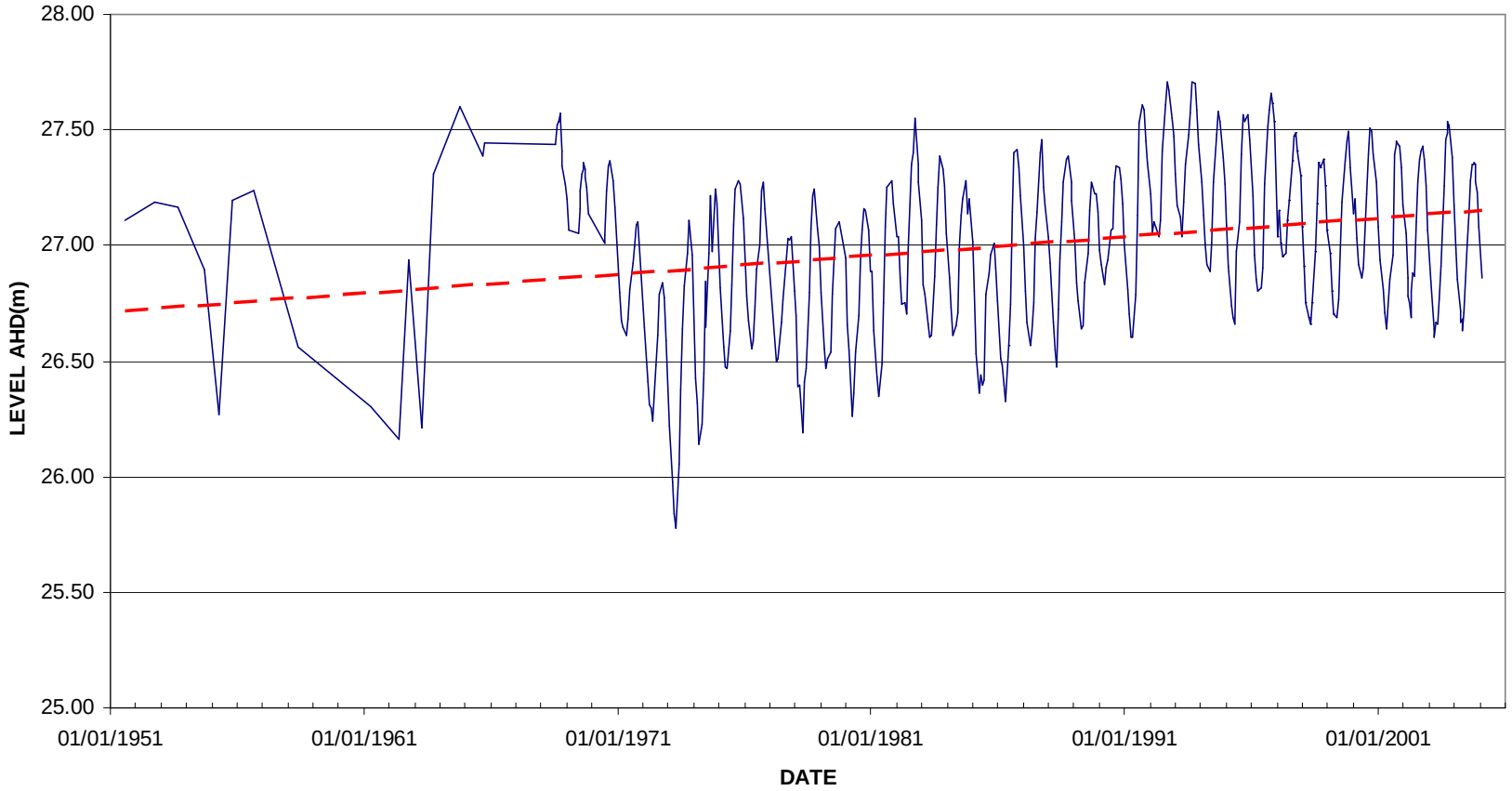
3.6a Pearson's correlations of Lake Goollelal peat elemental composition (n=6).

3.6b Pearson's correlations of Lake Goollelal floc elemental composition (n=6).

3.7 Lake Goollelal monitoring data (summer 1996 - autumn 2004) (Source: Clark and Horwitz, 2005).

Appendix 3.1: 6162517 LAKES AND WETLANDS LAKE GOOLLELAL 459

Easting = 387838.00 Northing = 6479242.00 Zone = 50 PM = 29.959mAHD WIN SITE ID = 14538



(Source: Western Australian Department of Environmental Protection)

APPENDIX 3.2:

Independent samples testing for differences in sediment characteristics between Lake Goollelal peat and floc sediments

		Levene's Test for Equality of Variances		t-test for Equality of Means						
		F	Sig.	t	df	Sig. (2-tailed)	Mean Difference	Std. Error Difference	95% Confidence Interval of the Difference	
									Lower	Upper
pH, direct	Equal variances assumed	4.136	0.069	-1.561	10	0.150	-0.290	0.186	-0.704	0.124
	Equal variances not assumed			-1.561	6.408	0.167	-0.290	0.186	-0.738	0.158
pH, 1:50	Equal variances assumed	3.078	0.110	-0.670	10	0.518	-0.138	0.206	-0.598	0.322
	Equal variances not assumed			-0.670	8.433	0.521	-0.138	0.206	-0.610	0.333
EC, 1:50	Equal variances assumed	0.361	0.561	-4.457	10	0.001***	-305.667	68.580	-458.473	-152.860
	Equal variances not assumed			-4.457	7.914	0.002**	-305.667	68.580	-464.111	-147.222
C	Equal variances assumed	0.312	0.589	1.820	10	0.099	2.767	1.520	-0.621	6.154
	Equal variances not assumed			1.820	8.551	0.104	2.767	1.520	-0.700	6.233
N	Equal variances assumed	5.708	0.038	-13.054	10	0.000***	-1.730	0.133	-2.025	-1.435
	Equal variances not assumed			-13.054	7.087	0.000***	-1.730	0.133	-2.043	-1.417
Na	Equal variances assumed	0.014	0.907	-2.581	10	0.027*	-0.038	0.015	-0.071	-0.005
	Equal variances not assumed			-2.581	9.972	0.027*	-0.038	0.015	-0.071	-0.005
Mg	Equal variances assumed	0.207	0.659	-1.708	10	0.118	-0.045	0.026	-0.104	0.014
	Equal variances not assumed			-1.708	9.958	0.119	-0.045	0.026	-0.104	0.014
Al	Equal variances assumed	3.969	0.074	-2.915	10	0.015*	-0.172	0.059	-0.303	-0.040
	Equal variances not assumed			-2.915	7.021	0.022*	-0.172	0.059	-0.311	-0.033
Si	Equal variances assumed	0.009	0.925	-1.883	10	0.089	-1.488	0.790	-3.249	0.273
	Equal variances not assumed			-1.883	9.999	0.089	-1.488	0.790	-3.249	0.273
P	Equal variances assumed	12.219	0.006	-9.330	10	0.000***	-0.227	0.024	-0.281	-0.173
	Equal variances not assumed			-9.330	5.428	0.000***	-0.227	0.024	-0.288	-0.166
S	Equal variances assumed	0.207	0.659	-2.637	10	0.025*	-1.412	0.535	-2.604	-0.219
	Equal variances not assumed			-2.637	9.920	0.025*	-1.412	0.535	-2.606	-0.218
K	Equal variances assumed	0.009	0.928	-16.734	10	0.000***	-0.170	0.010	-0.192	-0.147
	Equal variances not assumed			-16.734	9.965	0.000***	-0.170	0.010	-0.192	-0.147
Ca	Equal variances assumed	0.981	0.345	-1.123	10	0.288	-0.388	0.346	-1.159	0.382
	Equal variances not assumed			-1.123	9.060	0.290	-0.388	0.346	-1.170	0.393
Ti	Equal variances assumed	0.217	0.651	-5.687	10	0.000***	-0.019	0.003	-0.026	-0.011
	Equal variances not assumed			-5.687	8.920	0.000***	-0.019	0.003	-0.026	-0.011

		Levene's Test for Equality of Variances		t-test for Equality of Means						
		F	Sig.	t	df	Sig. (2-tailed)	Mean Difference	Std. Error Difference	95% Confidence Interval of the Lower	Upper
V	Equal variances assumed	2.663	0.134	3.322	10	0.008**	0.003	0.001	0.001	0.004
	Equal variances not assumed			3.322	6.997	0.013*	0.003	0.001	0.001	0.005
Cr	Equal variances assumed	11.769	0.006	2.328	10	0.042*	0.003	0.001	0.000	0.006
	Equal variances not assumed			2.328	5.717	0.061	0.003	0.001	0.000	0.007
Mn	Equal variances assumed	4.093	0.071	-7.217	10	0.000***	-0.005	0.001	-0.007	-0.004
	Equal variances not assumed			-7.217	6.328	0.000***	-0.005	0.001	-0.007	-0.003
Fe	Equal variances assumed	0.106	0.752	-0.841	10	0.420	-0.707	0.841	-2.580	1.167
	Equal variances not assumed			-0.841	9.905	0.420	-0.707	0.841	-2.582	1.169
Cu	Equal variances assumed	6.978	0.025	-5.383	10	0.000***	-0.004	0.001	-0.006	-0.003
	Equal variances not assumed			-5.383	5.372	0.002**	-0.004	0.001	-0.006	-0.002
Zn	Equal variances assumed	3.664	0.085	-4.311	10	0.002**	-0.004	0.001	-0.006	-0.002
	Equal variances not assumed			-4.311	7.608	0.003**	-0.004	0.001	-0.006	-0.002
As	Equal variances assumed	12.394	0.006	1.929	10	0.083	0.003	0.001	0.000	0.005
	Equal variances not assumed			1.929	5.204	0.109	0.003	0.001	-0.001	0.006
Rb	Equal variances assumed	0.597	0.457	-1.007	10	0.338	0.000	0.000	-0.001	0.000
	Equal variances not assumed			-1.007	9.204	0.340	0.000	0.000	-0.001	0.000
Sr	Equal variances assumed	0.730	0.413	-1.119	10	0.289	-0.001	0.001	-0.003	0.001
	Equal variances not assumed			-1.119	9.571	0.290	-0.001	0.001	-0.003	0.001
Ba	Equal variances assumed	0.357	0.564	0.090	10	0.930	0.000	0.002	-0.005	0.006
	Equal variances not assumed			0.090	9.222	0.930	0.000	0.002	-0.005	0.006
Pb	Equal variances assumed	3.450	0.093	-0.946	10	0.367	-0.002	0.002	-0.006	0.002
	Equal variances not assumed			-0.946	6.712	0.377	-0.002	0.002	-0.006	0.003

APPENDIX 3.3: Tests of Normality of elemental distribution within Lake Goollelal for peat and floc sediment

		Kolmogorov-Smirnov [a]			Shapiro-Wilk		
		Statistic	df	Sig.	Statistic	df	Sig.
pH	peat	0.302	6	0.092	0.806	6	0.067
	floc	0.255	6	0.200#	0.850	6	0.156
EC	peat	0.223	6	0.200#	0.930	6	0.578
	floc	0.367	6	0.011**	0.713	6	0.008**
C	peat	0.328	6	0.042*	0.802	6	0.062
	floc	0.224	6	0.200#	0.894	6	0.338
N	peat	0.226	6	0.200#	0.922	6	0.517
	floc	0.152	6	0.200#	0.950	6	0.742
Na	peat	0.307	6	0.080	0.735	6	0.014*
	floc	0.272	6	0.187	0.911	6	0.441
Mg	peat	0.242	6	0.200#	0.907	6	0.414
	floc	0.196	6	0.200#	0.941	6	0.668
Al	peat	0.157	6	0.200#	0.954	6	0.776
	floc	0.162	6	0.200#	0.945	6	0.696
Si	peat	0.243	6	0.200#	0.958	6	0.801
	floc	0.241	6	0.200#	0.801	6	0.060
P	peat	0.260	6	0.200#	0.884	6	0.288
	floc	0.199	6	0.200#	0.891	6	0.326
S	peat	0.300	6	0.097	0.866	6	0.211
	floc	0.258	6	0.200#	0.765	6	0.028*
K	peat	0.197	6	0.200#	0.915	6	0.472
	floc	0.114	6	0.200#	0.989	6	0.987
Ca	peat	0.287	6	0.133	0.822	6	0.092
	floc	0.261	6	0.200#	0.916	6	0.479
Ti	peat	0.209	6	0.200#	0.975	6	0.924
	floc	0.213	6	0.200#	0.962	6	0.837
Cr	peat	0.255	6	0.200#	0.841	6	0.132
	floc	0.188	6	0.200#	0.964	6	0.850
Mn	peat	0.245	6	0.200#	0.838	6	0.125
	floc	0.298	6	0.104	0.886	6	0.299
Fe	peat	0.226	6	0.200#	0.827	6	0.101
	floc	0.351	6	0.020	0.635	6	0.001***
Cu	peat	0.288	6	0.130	0.893	6	0.336
	floc	0.174	6	0.200#	0.973	6	0.911
Zn	peat	0.257	6	0.200#	0.932	6	0.596
	floc	0.274	6	0.178	0.858	6	0.184
As	peat	0.267	6	0.200#	0.818	6	0.085
	floc	0.321	6	0.052	0.829	6	0.106
Rb	peat	0.184	6	0.200#	0.937	6	0.634
	floc	0.130	6	0.200#	0.979	6	0.946
Sr	peat	0.205	6	0.200#	0.946	6	0.710
	floc	0.132	6	0.200#	0.983	6	0.967
Ba	peat	0.154	6	0.200#	0.970	6	0.895
	floc	0.272	6	0.189	0.924	6	0.532
Pb	peat	0.310	6	0.073	0.791	6	0.049*
	floc	0.188	6	0.200#	0.915	6	0.470

This is a lower bound of the true significance.

a Lilliefors Significance Correction

APPENDIX 3.4: Comparison of Lake Goollelal sediment total elemental composition by XRF, Aqua Regia/ICP-AES, Total S Analyser, sequential extraction schemes (Hall et al., 1996 and Ruttenberg, 1992), and Davis et al. (1993)

	Al					As					Ca				
	XRF %	**AR-ICP %**	**Hall**	**Ruttenberg**	**Davis *et al.***	**XRF %**	**AR-ICP ppm**	**Hall**	**Ruttenberg**	**Davis *et al.***	**XRF %**	**AR-ICP %**	**Hall**	**Ruttenberg**	**Davis *et al.***
Sample					0.4/1.3%					45/225 ppm					1.3/0.9%
Site 1 peat	0.43	0.35					44								
Site 1 floc	0.61	0.42					28				1.80	1.69			
Site 2 peat	0.56	0.49					102				2.71	2.61			
Site 2 floc	0.48	0.34					22				1.39	1.53			
Site 3 peat	0.32	0.27	0.33	0.15			25				1.74	1.63			
Site 3 floc	0.59	0.55	0.49	0.31			22				1.96	1.79	1.80	1.97	
Site 4 peat	0.21	0.18					26				1.69	1.93	1.60	1.86	
Site 4 floc	0.55	0.38					20				2.05	1.84			
Site 5 peat	0.24	0.20					25				1.87	1.67			
Site 5 floc	0.51	0.35					31				1.93	1.75			
Site 6 peat	0.41	0.34	0.36	0.22			74				3.02	2.78			
Site 6 floc	0.46	0.30	0.40	0.20			20				0.76	0.76	0.91	1.00	
Mean peat	**0.36**	**0.30**	**0.35**	**0.18**			**49**				1.19	0.95	0.98	1.20	
Mean floc	**0.53**	**0.39**	**0.45**	**0.26**			**24**				**1.65**	**1.56**	**1.36**	**1.49**	

	Cu					Fe					K	
	XRFppm	**AR-ICPppm**			**Davis *et al.***	**XRF %**	**AR-ICP %**	**Hall**	**Ruttenberg**	**Davis *et al.***	**XRF %**	**AR-ICP %**
Sample					5/9 ppm					4.1/5.5%		
Site 1 peat		8.53				2.19	1.91				0.104	0.082
Site 1 floc	21.72	52.21				3.02	2.61				0.283	0.162
Site 2 peat		8.06				3.46	3.61				0.088	0.061
Site 2 floc	7.28	24.30				2.99	2.43				0.242	0.181
Site 3 peat		15.01				2.78	2.31	2.56	1.17		0.078	0.079
Site 3 floc	40.36	78.78				2.97	3.15	2.80	0.55		0.266	0.256
Site 4 peat		13.48				1.75	1.49				0.078	0.067
Site 4 floc	37.34	61.79				3.17	2.67				0.250	0.200
Site 5 peat		5.35				2.01	1.68				0.104	0.078
Site 5 floc	43.53	62.65				3.65	3.13				0.258	0.158
Site 6 peat		7.61				5.86	4.95	5.27	1.73		0.060	0.048
Site 6 floc	17.61	38.33				6.49	4.67	6.48	1.09		0.232	0.148
Mean peat		**9.67**				**3.01**	**2.66**	**3.91**	**1.45**		**0.09**	**0.07**
Mean floc	**27.97**	**53.01**				**3.71**	**3.11**	**4.64**	**0.82**		**0.26**	**0.18**

	Mg					Mn					Na				
	XRF %	**AR-ICP %**	**Hall**	**Ruttenberg**	**Davis *et al.***	**XRFppm**	**AR-ICPppm**	**Hall**		**Davis *et al.***	**XRF %**	**AR-ICP %**	**Hall**	**Ruttenberg**	**Davis *et al.***
Sample					0.3/0.2%					20/20 ppm					0.3/0.1%
Site 1 peat	0.22	0.30					20.88				0.10	0.43			
Site 1 floc	0.29	0.35				8.01	83.53				0.13	0.50			
Site 2 peat	0.17	0.28					23.33				0.09	0.36			
Site 2 floc	0.28	0.34				8.05	69.17				0.12	0.48			
Site 3 peat	0.32	0.37					32.71	32			0.09	0.52			
Site 3 floc	0.32	0.43				16.03	88.62	65			0.13	0.43			
Site 4 peat	0.31	0.36					33.69				0.15	0.35			
Site 4 floc	0.33	0.37				24.10	95.18				0.15	0.60			
Site 5 peat	0.26	0.29					30.31				0.08	0.28			
Site 5 floc	0.29	0.33				16.05	83.53				0.18	0.40			
Site 6 peat	0.17	0.25					20.93	20			0.08	0.51			
Site 6 floc	0.30	0.28					50.00	17			0.11	0.30			
Mean peat	**0.24**	**0.30**					**26.98**	**26**			**0.10**	**0.41**			
Mean floc	**0.30**	**0.35**					**78.34**	**41**			**0.14**	**0.45**			

	P					Pb	S					
	XRF %	**AR-ICP %**	**Hall**	**Ruttenberg**	**Davis *et al.***	**AR-ICPppm**	**XRF %**	**AR-ICP %**	**Hall**	**TS analyser**	**Cr-red. S%**	**$KClO_3$-S %**
Sample					0.02/0.18%							
Site 1 peat	0.04	0.04				31.32	0.42	3.31		3.86		
Site 1 floc	0.20	0.19				71.35	0.48	4.70		5.35		
Site 2 peat	0.06	0.06				14.84	0.59	3.61		4.12		
Site 2 floc	0.25	0.24				50.47	0.50	4.67		5.33		
Site 3 peat	0.05	0.04		0.03		23.09	0.65	4.62	4.20	5.12	1.46	3.00
Site 3 floc	0.33	0.37		0.23		86.65	0.92	5.71	4.32	5.26	1.55	3.32
Site 4 peat	0.03	0.03				69.37	0.59	3.57		4.02		
Site 4 floc	0.28	0.25				85.16	0.57	4.84		5.68		
Site 5 peat	0.03	0.03				17.83	0.59	3.21		3.57		
Site 5 floc	0.21	0.19				57.43	0.64	5.22		6.10		
Site 6 peat	0.05	0.04		0.03		127.49	0.96	6.47	5.60	6.13	1.45	4.74
Site 6 floc	0.34	0.27		0.22		43.34	0.54	6.83	7.89	7.57	4.04	7.03
Mean peat	**0.04**	**0.04**		**0.03**		**47.33**	**0.63**	**4.13**	**4.90**	**4.47**	**1.46**	**3.87**
Mean floc	**0.27**	**0.25**		**0.23**		**65.73**	**0.61**	**5.33**	**6.10**	**5.88**	**2.80**	**5.18**

	Zn				
	XRF %	**AR-ICP %**	**Hall**	**Ruttenberg**	**Davis *et al.***
Sample					18/18
Site 1 peat		19.14			
Site 1 floc	48.60	85.27			
Site 2 peat		23.33			
Site 2 floc	41.58	78.52			
Site 3 peat		42.33			
Site 3 floc	86.92	137.86			
Site 4 peat		21.80			
Site 4 floc	86.10	111.88			
Site 5 peat		14.26			
Site 5 floc	58.04	92.23			
Site 6 peat	2.08	32.35			
Site 6 floc	56.99	66.67			
Mean peat		**25.54**			
Mean floc	**63.04**	**95.40**			

APPENDIX 3.5:

Some elemental concentrations (mg L^{-1}) of water drained from Lake Goollelal floc taken from six locations around the lake.

Site	Al	Ca	Cd	Cu	Fe	K	Mg	Mn	Na	P	S	Zn
1	0.02	110	-	0.070	0.062	22	39	0.059	120	0.140	17	0.210
2	0.02	110	-	0.050	0.047	24	41	0.060	120	0.140	17	0.150
3	0.02	95	-	0.051	0.055	19	40	0.036	120	0.270	18	0.180
4	0.01	100	-	0.062	0.057	20	38	0.040	130	0.220	16	0.220
5	0.01	120	0.0093	0.046	0.049	24	39	0.047	120	0.110	29	0.270
6	0.02	42	-	0.031	0.100	9	22	0.037	95	0.070	16	0.140
Mean	**0.02**	**96**		**0.052**	**0.062**	**20**	**37**	**0.047**	**118**	**0.158**	**19**	**0.195**
S.E.	**0.002**	**11**		**0.005**	**0.008**	**2**	**3**	**0.004**	**5**	**0.030**	**2**	**0.020**

APPENDIX 3.6a: Pearson's correlations of Lake Goollelal peat elemental composition (n=6)

		Northings	Eastings	pH direct	pH diluted	EC direct	EC diluted	C	N	Na	Mg	Al	Si	P	S	K	Ca	Ti	V
Eastings	Pearson Correlation	-0.768																	
	Sig. (2-tailed)	0.075																	
pH direct	Pearson Correlation	-0.783	0.274																
	Sig. (2-tailed)	0.066	0.599																
pH diluted	Pearson Correlation	-0.580	-0.048	0.897															
	Sig. (2-tailed)	0.228	0.929	0.015*															
EC direct	Pearson Correlation	0.226	0.329	-0.999	-0.691														
	Sig. (2-tailed)	0.855	0.787	0.03*	0.515														
EC diluted	Pearson Correlation	-0.754	0.416	0.813	0.740	-0.916													
	Sig. (2-tailed)	0.083	0.413	0.049*	0.093	0.263													
C	Pearson Correlation	-0.617	0.254	0.890	0.651	-0.896	0.631												
	Sig. (2-tailed)	0.192	0.627	0.017*	0.162	0.292	0.179												
N	Pearson Correlation	-0.750	0.751	0.625	0.373	-0.709	0.708	0.602											
	Sig. (2-tailed)	0.086	0.085	0.185	0.466	0.498	0.116	0.206											
Na	Pearson Correlation	-0.504	0.087	0.532	0.493	-0.356	0.467	0.421	-0.081										
	Sig. (2-tailed)	0.309	0.870	0.277	0.321	0.768	0.350	0.405	0.879										
Mg	Pearson Correlation	-0.875	0.473	0.777	0.774	-0.246	0.862	0.456	0.551	0.609									
	Sig. (2-tailed)	0.023*	0.343	0.069	0.071	0.842	0.027*	0.363	0.257	0.200									
Al	Pearson Correlation	0.670	-0.182	-0.915	-0.788	0.884	-0.512	-0.886	-0.480	-0.444	-0.557								
	Sig. (2-tailed)	0.146	0.730	0.010**	0.063	0.310	0.299	0.019*	0.336	0.377	0.251								
Si	Pearson Correlation	0.800	-0.372	-0.954	-0.747	0.930	-0.738	-0.943	-0.593	-0.631	-0.694	0.908							
	Sig. (2-tailed)	0.056	0.468	0.003**	0.088	0.240	0.094	0.005**	0.215	0.179	0.126	0.01*							
P	Pearson Correlation	0.332	0.210	-0.730	-0.695	0.979	-0.230	-0.757	-0.065	-0.495	-0.291	0.898	0.742						
	Sig. (2-tailed)	0.521	0.689	0.099	0.125	0.132	0.660	0.082	0.902	0.318	0.575	0.015*	0.091						
S	Pearson Correlation	-0.184	0.712	-0.178	-0.564	-0.055	-0.016	0.098	0.508	-0.319	-0.213	0.189	0.001	0.430					
	Sig. (2-tailed)	0.728	0.113	0.736	0.244	0.965	0.976	0.854	0.303	0.538	0.686	0.720	0.998	0.395					
K	Pearson Correlation	0.391	-0.797	0.059	0.469	-0.206	0.001	-0.165	-0.383	-0.083	0.018	-0.024	0.185	-0.227	-0.880				
	Sig. (2-tailed)	0.444	0.058	0.912	0.348	0.868	0.998	0.755	0.454	0.876	0.973	0.963	0.726	0.666	0.010*				
Ca	Pearson Correlation	-0.502	-0.108	0.727	0.941	-0.240	0.648	0.367	0.202	0.487	0.798	-0.594	-0.537	-0.525	-0.716	0.587			
	Sig. (2-tailed)	0.310	0.838	0.101	0.005**	0.846	0.164	0.474	0.701	0.328	0.057	0.214	0.272	0.284	0.110	0.221			
Ti	Pearson Correlation	0.763	-0.219	-0.973	-0.890	0.971	-0.817	-0.849	-0.489	-0.708	-0.808	0.864	0.953	0.730	0.254	-0.062	-0.748		
	Sig. (2-tailed)	0.078	0.676	0.001**	0.018*	0.154	0.047*	0.033*	0.325	0.116	0.052	0.026*	0.003**	0.099	0.627	0.907	0.087		
V	Pearson Correlation	0.293	0.250	-0.817	-0.831	0.987	-0.510	-0.811	-0.325	-0.254	-0.356	0.827	0.722	0.833	0.401	-0.433	-0.630	0.762	
	Sig. (2-tailed)	0.573	0.632	0.047*	0.040*	0.102	0.301	0.050*	0.529	0.627	0.488	0.042*	0.105	0.039*	0.431	0.391	0.180	0.078	
Cr	Pearson Correlation	0.598	-0.047	-0.929	-0.957	0.918	-0.732	-0.759	-0.553	-0.302	-0.690	0.852	0.784	0.703	0.378	-0.372	-0.828	0.861	0.897
	Sig. (2-tailed)	0.210	0.930	0.007**	0.003**	0.260	0.098	0.080	0.255	0.561	0.129	0.031*	0.065	0.119	0.459	0.468	0.042*	0.028*	0.015*
Mn	Pearson Correlation	-0.868	0.444	0.801	0.757	0.935	0.571	0.546	0.504	0.490	0.838	-0.802	-0.742	-0.585	-0.235	-0.019	0.738	-0.772	-0.463
	Sig. (2-tailed)	0.025*	0.378	0.056	0.082	0.232	0.236	0.263	0.308	0.324	0.037	0.050*	0.091	0.223	0.655	0.971	0.094	0.072	0.355
Fe	Pearson Correlation	0.291	0.344	-0.596	-0.879	0.187	-0.492	-0.254	0.049	-0.508	-0.649	0.493	0.408	0.541	0.866	-0.723	-0.965	0.650	0.607
	Sig. (2-tailed)	0.576	0.505	0.211	0.021	0.880	0.321	0.627	0.927	0.304	0.163	0.320	0.422	0.268	0.025*	0.104	0.002**	0.162	0.202
Cu	Pearson Correlation	-0.882	0.742	0.576	0.432	-0.368	0.814	0.359	0.620	0.569	0.887	-0.315	-0.592	0.013	0.193	-0.380	0.439	-0.624	-0.028
	Sig. (2-tailed)	0.020*	0.091	0.231	0.392	0.760	0.049*	0.484	0.189	0.238	0.018*	0.543	0.216	0.981	0.715	0.457	0.383	0.185	0.959
Zn	Pearson Correlation	-0.561	0.919	0.087	-0.185	0.145	0.410	0.077	0.760	-0.163	0.335	0.093	-0.137	0.501	0.785	-0.702	-0.226	-0.013	0.355
	Sig. (2-tailed)	0.246	0.010**	0.869	0.725	0.907	0.419	0.884	0.079	0.758	0.517	0.860	0.795	0.311	0.064	0.120	0.667	0.980	0.490
As	Pearson Correlation	0.645	-0.118	-0.964	-0.928	0.984	-0.756	-0.846	-0.606	-0.344	-0.682	0.894	0.858	0.732	0.273	-0.252	-0.760	0.899	0.907
	Sig. (2-tailed)	0.166	0.823	0.002**	0.007**	0.114	0.082	0.033*	0.203	0.504	0.136	0.016*	0.028*	0.098	0.601	0.630	0.079	0.015*	0.013*
Rb	Pearson Correlation	-0.431	0.188	0.172	0.255	0.969	-0.032	-0.100	-0.195	0.532	0.468	-0.278	-0.182	-0.284	-0.392	-0.024	0.429	-0.252	0.134
	Sig. (2-tailed)	0.394	0.722	0.745	0.626	0.158	0.952	0.851	0.712	0.277	0.349	0.594	0.729	0.585	0.442	0.964	0.396	0.630	0.800
Sr	Pearson Correlation	-0.545	-0.073	0.733	0.819	-0.194	0.493	0.507	0.000	0.837	0.713	-0.714	-0.701	-0.754	-0.633	0.288	0.824	-0.831	-0.576
	Sig. (2-tailed)	0.263	0.890	0.097	0.046*	0.875	0.320	0.305	0.999	0.038	0.112	0.111	0.121	0.084	0.178	0.579	0.044*	0.040*	0.231
Ba	Pearson Correlation	-0.529	0.344	0.672	0.558	-0.994	0.904	0.623	0.778	0.135	0.580	-0.374	-0.593	-0.092	0.188	-0.012	0.395	-0.620	-0.522
	Sig. (2-tailed)	0.281	0.505	0.144	0.250	0.070	0.013*	0.186	0.068	0.799	0.228	0.465	0.214	0.863	0.721	0.981	0.438	0.189	0.289
Pb	Pearson Correlation	-0.055	0.338	-0.027	-0.427	-0.288	-0.127	0.383	0.145	0.111	-0.334	-0.083	-0.250	-0.083	0.729	-0.787	-0.667	0.012	0.092
	Sig. (2-tailed)	0.918	0.513	0.960	0.398	0.814	0.811	0.453	0.784	0.834	0.518	0.876	0.633	0.875	0.101	0.063	0.148	0.983	0.862

* Correlation is significant at the 0.05 level (2-tailed).

** Correlation is significant at the 0.01 level (2-tailed).

		Cr	Mn	Fe	Cu	Zn	As	Rb	Sr	Ba
Eastings	Pearson Correlation									
	Sig. (2-tailed)									
pH direct	Pearson Correlation									
	Sig. (2-tailed)									
pH diluted	Pearson Correlation									
	Sig. (2-tailed)									
EC direct	Pearson Correlation									
	Sig. (2-tailed)									
EC diluted	Pearson Correlation									
	Sig. (2-tailed)									
C	Pearson Correlation									
	Sig. (2-tailed)									
N	Pearson Correlation									
	Sig. (2-tailed)									
Na	Pearson Correlation									
	Sig. (2-tailed)									
Mg	Pearson Correlation									
	Sig. (2-tailed)									
Al	Pearson Correlation									
	Sig. (2-tailed)									
Si	Pearson Correlation									
	Sig. (2-tailed)									
P	Pearson Correlation									
	Sig. (2-tailed)									
S	Pearson Correlation									
	Sig. (2-tailed)									
K	Pearson Correlation									
	Sig. (2-tailed)									
Ca	Pearson Correlation									
	Sig. (2-tailed)									
Ti	Pearson Correlation									
	Sig. (2-tailed)									
V	Pearson Correlation									
	Sig. (2-tailed)									
Cr	Pearson Correlation									
	Sig. (2-tailed)									
Mn	Pearson Correlation	-0.737								
	Sig. (2-tailed)	0.095								
Fe	Pearson Correlation	0.725	-0.591							
	Sig. (2-tailed)	0.103	0.217							
Cu	Pearson Correlation	-0.371	0.633	-0.259						
	Sig. (2-tailed)	0.469	0.177	0.621						
Zn	Pearson Correlation	0.069	0.165	0.453	0.651					
	Sig. (2-tailed)	0.897	0.755	0.366	0.162					
As	Pearson Correlation	0.989	-0.733	0.645	-0.406	0.014				
	Sig. (2-tailed)	0.000**	0.097	0.167	0.424	0.978				
Rb	Pearson Correlation	-0.088	0.663	-0.424	0.344	-0.120	-0.052			
	Sig. (2-tailed)	0.869	0.151	0.402	0.505	0.821	0.922			
Sr	Pearson Correlation	-0.664	0.757	-0.832	0.437	-0.356	-0.654	0.637		
	Sig. (2-tailed)	0.150	0.081	0.040*	0.387	0.488	0.159	0.174		
Ba	Pearson Correlation	-0.644	0.274	-0.239	0.583	0.463	-0.680	-0.443	0.147	
	Sig. (2-tailed)	0.167	0.600	0.648	0.224	0.356	0.137	0.378	0.781	
Pb	Pearson Correlation	0.308	-0.252	0.699	-0.017	0.256	0.164	-0.306	-0.260	0.011
	Sig. (2-tailed)	0.553	0.630	0.122	0.974	0.624	0.756	0.555	0.619	0.984

***** Correlation is significant at the 0.05 level (2-tailed).

****** Correlation is significant at the 0.01 level (2-tailed).

APPENDIX 3.6b: Pearson's correlations of Lake Goollelal floc elemental composition (n=6)

		Northings	Eastings	pH direct	pH diluted	EC direct	EC diluted	C	N	Na	Mg	Al	Si	P	S	K	Ca	Ti	V
Eastings	Pearson Correlation	-0.768																	
	Sig. (2-tailed)	0.075																	
pH direct	Pearson Correlation	-0.089	-0.487																
	Sig. (2-tailed)	0.886	0.405																
pH diluted	Pearson Correlation	-0.085	-0.435	0.982															
	Sig. (2-tailed)	0.873	0.388	0.003**															
EC direct	Pearson Correlation	-0.132	-0.408	0.992	0.962														
	Sig. (2-tailed)	0.802	0.422	0.001**	0.002**														
EC diluted	Pearson Correlation	-0.246	-0.372	0.985	0.914	0.970													
	Sig. (2-tailed)	0.639	0.467	0.002**	0.010**	0.001**													
C	Pearson Correlation	-0.685	0.415	0.152	0.295	0.161	0.214												
	Sig. (2-tailed)	0.133	0.413	0.808	0.570	0.761	0.683												
N	Pearson Correlation	-0.743	0.736	-0.098	0.061	-0.037	-0.047	0.871											
	Sig. (2-tailed)	0.091	0.095	0.875	0.909	0.944	0.930	0.024*											
Na	Pearson Correlation	-0.170	-0.378	0.699	0.510	0.678	0.782	-0.029	-0.283										
	Sig. (2-tailed)	0.747	0.460	0.189	0.301	0.139	0.066	0.956	0.586										
Mg	Pearson Correlation	-0.769	0.539	0.449	0.481	0.489	0.482	0.504	0.614	0.066									
	Sig. (2-tailed)	0.074	0.270	0.448	0.334	0.325	0.332	0.309	0.195	0.901									
Al	Pearson Correlation	-0.389	-0.009	0.716	0.641	0.589	0.634	0.303	0.129	0.155	0.718								
	Sig. (2-tailed)	0.446	0.987	0.174	0.170	0.219	0.176	0.559	0.807	0.770	0.108								
Si	Pearson Correlation	0.750	-0.291	-0.338	-0.373	-0.303	-0.435	-0.912	-0.664	-0.292	-0.499	-0.449							
	Sig. (2-tailed)	0.086	0.575	0.578	0.467	0.559	0.388	0.010**	0.151	0.574	0.314	0.371							
P	Pearson Correlation	-0.575	0.947	-0.743	-0.688	-0.679	-0.639	0.288	0.611	-0.536	0.257	-0.222	-0.138						
	Sig. (2-tailed)	0.233	0.004**	0.150	0.131	0.138	0.172	0.580	0.197	0.273	0.624	0.672	0.794						
S	Pearson Correlation	0.203	0.134	-0.866	-0.906	-0.841	-0.735	-0.356	-0.302	-0.193	-0.702	-0.671	0.302	0.407					
	Sig. (2-tailed)	0.699	0.800	0.058	0.013*	0.036*	0.096	0.489	0.561	0.714	0.120	0.144	0.561	0.423					
K	Pearson Correlation	-0.060	-0.328	0.797	0.692	0.680	0.696	-0.049	-0.244	0.280	0.500	0.917	-0.144	-0.513	-0.646				
	Sig. (2-tailed)	0.910	0.526	0.106	0.127	0.138	0.125	0.927	0.641	0.591	0.312	0.010**	0.785	0.298	0.166				
Ca	Pearson Correlation	0.289	-0.770	0.827	0.678	0.764	0.794	-0.333	-0.639	0.762	-0.036	0.406	0.042	-0.890	-0.381	0.676			
	Sig. (2-tailed)	0.579	0.073	0.084	0.139	0.077	0.059	0.519	0.172	0.078	0.946	0.425	0.937	0.018*	0.457	0.140			
Ti	Pearson Correlation	0.044	-0.550	0.900	0.849	0.805	0.818	0.073	-0.246	0.427	0.353	0.827	-0.263	-0.730	-0.702	0.929	0.794		
	Sig. (2-tailed)	0.933	0.258	0.037*	0.032*	0.053	0.046*	0.891	0.638	0.398	0.492	0.042*	0.614	0.099	0.120	0.007**	0.059		
V	Pearson Correlation	0.437	-0.164	.	0.149	0.061	-0.164	-0.032	0.161	-0.326	-0.148	-0.434	0.372	-0.151	-0.306	-0.357	-0.211	-0.225	
	Sig. (2-tailed)	0.386	0.756	.	0.779	0.909	0.757	0.952	0.761	0.528	0.780	0.390	0.468	0.775	0.556	0.488	0.688	0.669	
Cr	Pearson Correlation	0.351	-0.171	-0.550	-0.606	-0.541	-0.478	-0.258	-0.302	0.112	-0.844	-0.869	0.229	0.064	0.817	-0.779	-0.166	-0.635	0.036
	Sig. (2-tailed)	0.495	0.746	0.337	0.202	0.268	0.338	0.621	0.561	0.832	0.034*	0.025*	0.663	0.905	0.047*	0.068	0.754	0.176	0.946
Mn	Pearson Correlation	-0.565	-0.045	0.892	0.841	0.856	0.918	0.526	0.294	0.619	0.713	0.761	-0.707	-0.335	-0.751	0.662	0.525	0.738	-0.284
	Sig. (2-tailed)	0.243	0.932	0.042*	0.036*	0.030*	0.010**	0.284	0.572	0.191	0.112	0.079	0.116	0.517	0.086	0.152	0.285	0.094	0.586
Fe	Pearson Correlation	0.216	0.208	-0.930	-0.958	-0.917	-0.834	-0.365	-0.256	-0.360	-0.658	-0.643	0.362	0.490	0.983	-0.636	-0.486	-0.734	-0.257
	Sig. (2-tailed)	0.681	0.693	0.022*	0.003**	0.010**	0.039*	0.477	0.625	0.483	0.156	0.168	0.480	0.323	0.000**	0.175	0.328	0.097	0.623
Cu	Pearson Correlation	-0.767	0.358	0.616	0.307	0.434	0.578	0.249	0.186	0.511	0.718	0.674	-0.525	0.133	-0.283	0.546	0.292	0.399	-0.726
	Sig. (2-tailed)	0.075	0.486	0.269	0.554	0.390	0.229	0.634	0.724	0.300	0.108	0.142	0.285	0.802	0.587	0.262	0.574	0.433	0.102
Zn	Pearson Correlation	-0.990	0.716	0.098	0.069	0.120	0.262	0.673	0.678	0.224	0.713	0.410	-0.785	0.538	-0.140	0.089	-0.232	-0.006	-0.546
	Sig. (2-tailed)	0.000**	0.110	0.875	0.896	0.821	0.616	0.143	0.139	0.669	0.112	0.419	0.065	0.271	0.791	0.867	0.658	0.990	0.262
As	Pearson Correlation	0.429	-0.744	0.642	0.466	0.593	0.604	-0.616	-0.815	0.657	-0.155	0.264	0.335	-0.813	-0.207	0.602	0.946	0.641	-0.196
	Sig. (2-tailed)	0.396	0.090	0.243	0.352	0.215	0.204	0.193	0.048*	0.156	0.769	0.614	0.517	0.049*	0.693	0.207	0.004**	0.170	0.710
Rb	Pearson Correlation	-0.280	0.586	-0.192	-0.172	-0.047	-0.165	-0.139	0.322	-0.144	0.393	-0.264	0.312	0.483	-0.122	-0.300	-0.384	-0.480	0.398
	Sig. (2-tailed)	0.591	0.222	0.757	0.744	0.930	0.755	0.792	0.534	0.785	0.441	0.614	0.547	0.331	0.818	0.563	0.453	0.335	0.435
Sr	Pearson Correlation	-0.656	0.032	0.729	0.618	0.679	0.807	0.580	0.316	0.766	0.516	0.485	-0.814	-0.204	-0.437	0.353	0.430	0.478	-0.410
	Sig. (2-tailed)	0.157	0.951	0.162	0.191	0.138	0.052	0.228	0.542	0.076	0.295	0.329	0.049*	0.699	0.387	0.493	0.395	0.337	0.419
Ba	Pearson Correlation	0.227	-0.578	0.613	0.386	0.392	0.481	-0.298	-0.621	0.345	-0.011	0.650	0.000	-0.611	-0.166	0.824	0.757	0.802	-0.576
	Sig. (2-tailed)	0.665	0.229	0.271	0.450	0.442	0.334	0.566	0.188	0.503	0.983	0.163	1.000	0.198	0.753	0.043*	0.082	0.055	0.231
Pb	Pearson Correlation	-0.793	0.349	0.601	0.574	0.543	0.623	0.687	0.562	0.248	0.877	0.838	-0.794	0.089	-0.633	0.593	0.131	0.547	-0.413
	Sig. (2-tailed)	0.060	0.498	0.284	0.234	0.265	0.186	0.132	0.245	0.636	0.022	0.037	0.059	0.867	0.177	0.215	0.805	0.262	0.416

* Correlation is significant at the 0.05 level (2-tailed).

** Correlation is significant at the 0.01 level (2-tailed).

		Cr	Mn	Fe	Cu	Zn	As	Rb	Sr	Ba
Eastings	Pearson Correlation									
	Sig. (2-tailed)									
pH direct	Pearson Correlation									
	Sig. (2-tailed)									
pH diluted	Pearson Correlation									
	Sig. (2-tailed)									
EC direct	Pearson Correlation									
	Sig. (2-tailed)									
EC diluted	Pearson Correlation									
	Sig. (2-tailed)									
C	Pearson Correlation									
	Sig. (2-tailed)									
N	Pearson Correlation									
	Sig. (2-tailed)									
Na	Pearson Correlation									
	Sig. (2-tailed)									
Mg	Pearson Correlation									
	Sig. (2-tailed)									
Al	Pearson Correlation									
	Sig. (2-tailed)									
Si	Pearson Correlation									
	Sig. (2-tailed)									
P	Pearson Correlation									
	Sig. (2-tailed)									
S	Pearson Correlation									
	Sig. (2-tailed)									
K	Pearson Correlation									
	Sig. (2-tailed)									
Ca	Pearson Correlation									
	Sig. (2-tailed)									
Ti	Pearson Correlation									
	Sig. (2-tailed)									
V	Pearson Correlation									
	Sig. (2-tailed)									
Cr	Pearson Correlation									
	Sig. (2-tailed)									
Mn	Pearson Correlation	-0.609								
	Sig. (2-tailed)	0.199								
Fe	Pearson Correlation	0.731	-0.821							
	Sig. (2-tailed)	0.099	0.045*							
Cu	Pearson Correlation	-0.485	0.727	-0.328						
	Sig. (2-tailed)	0.330	0.101	0.525						
Zn	Pearson Correlation	-0.302	0.576	-0.166	0.802					
	Sig. (2-tailed)	0.560	0.231	0.753	0.055					
As	Pearson Correlation	-0.081	0.284	-0.291	0.212	-0.379				
	Sig. (2-tailed)	0.879	0.586	0.576	0.687	0.459				
Rb	Pearson Correlation	-0.148	-0.138	-0.068	0.080	0.166	-0.240			
	Sig. (2-tailed)	0.779	0.795	0.898	0.881	0.753	0.646			
Sr	Pearson Correlation	-0.237	0.901	-0.559	0.726	0.694	0.183	-0.174		
	Sig. (2-tailed)	0.651	0.014*	0.248	0.102	0.126	0.729	0.742		
Ba	Pearson Correlation	-0.316	0.360	-0.197	0.365	-0.134	0.736	-0.651	0.203	
	Sig. (2-tailed)	0.542	0.483	0.709	0.476	0.800	0.095	0.161	0.699	
Pb	Pearson Correlation	-0.734	0.875	-0.638	0.794	0.796	-0.089	-0.060	0.756	0.238
	Sig. (2-tailed)	0.097	0.023	0.173	0.059	0.058	0.867	0.910	0.082	0.649

***** Correlation is significant at the 0.05 level (2-tailed).

****** Correlation is significant at the 0.01 level (2-tailed).

APPENDIX 3.7:

Lake Goollelal monitoring data (summer 1996 - autumn 2004). R= sampling round; odd numbers= summer/autumn, even numbers= spring (Source: Clark and Horwitz, 2005)

Round	Year	Depth (cm)	pH range	EC range ($\mu S\ cm^{-1}$)	Temp. range (^oC)	Dissolved oxygen ($mg\ L^{-1}$)	Chlorophyll *a* ($\mu g\ L^{-1}$)	Turbidity (FTU)	Gilvin (g440)	NO_3+NO_2-N ($\mu g\ L^{-1}$)	NH_4-N ($\mu g\ L^{-1}$)	TKN ($\mu g\ L^{-1}$)	PO_4-P ($\mu g\ L^{-1}$)	TP ($\mu g\ L^{-1}$)
R1	1996	38.3	7.20-9.30	1213-1295	18.6-23.5	7.8-10.7	27	9	5	1	98	1683	56	74
R2	1996	100.0	7.89-8.71	649-709	19.1-20.5	3.08-8.60		5	4	2	10	1789	7	88
R3	1997	27.7	9.37-9.58	1103-1115	24.8-25.5	7.0-8.2	6	13	8	8	31	1374	12	42
R4	1997	65.2	7.58-8.52	830-870	20.5-22.8	6.49-10.20		8	4	21	7	771	5	20
R5	1998	21-43	8.65-9.18	1472-1505	22.7-22.9	6.68-8.55	25	30	7	2	12	2339	3	66
R6	1998	85-90	7.67-8.12	807	17.20-17.53	2.0-2.7	0.43	2-4	7	3	8	644	<2	17
R7	1999	25-48	9.16-9.68	1471-1529	25.22-27.75	7.1-11.3	11	25-37	7	3	10	2258	5	57
R8	1999	50-120	7.4-8.39	837-880	20.2-22.5	2.54-9.20	0.04	8	10	<2	7	882	3	20
R9	2000	34-95	7.49- 9.02	960-990	20.0- 22.3	1.84-4.40	3	1	3	2	89	1360	7	27
R10	2000	45-80	8.53-9.07	791-796	20.3-20.4	6.3-7.5		17	31	5	7	1163	5	45
R11	2001	20	7.95-9.33	1453-1535	23.7-25.5	3.8-7.5		29	4	5	6	2309	7	67
R12	2001	55-90	7.49-7.87	707-735	17.21-19.18	4.1-9.4	2	3	14	7	8	700	5	21
R13	2002	20-50	8.66-9.24	1155-1191	22.2-23.1	5.1-6.0	1	5	0.2	31	13	1100	8	27
R14	2002	45-75	7.57-8.43	922-938	16.4-17.8	6.58-8.65	32	8	1	17	8	1100	5	37
R15	2003	15-50	7.30-9.08	1080-1499	20.1-22.5	3.72-9.41	14	20	1	120	37	1400	8	48
R16	2003	32-145	7.51 - 8.35	813 - 818	18.9 - 19.8	6.25 - 9.68	2	15	2	3	6	610	6	14
R17	2004	15-19	8.6 - 8.8	1195 - 1229	25.2 - 27.7		22			21	15	1000	15	32
R18	2004	52 - 95	7.76 - 8.09	937 - 955	20.3 - 20.6	6.75 - 7.77	4	11	1	38	28	750	17	22

Chapter 4

4.1 One-way ANOVA table testing the significance of the differences in water:sediment ratios (peat and floc combined) between treatments on individual sampling days

4.2 One-way ANOVAs for peat on individual days per combination of treatment and incubation type.

4.3a Spearman's rank order correlations between dependent variables over time (n=4), and on individual sampling days (n=6, Sites 1-6).
4.3b Spearman's rank order correlations between dependent variables over time (n=4), and on individual sampling days (n=5, Sites 1-5).

4.4 ORP in the floc incubations.

4.5 One-way ANOVAs for floc on individual days per combination of treatment and incubation type.

Appendix 4.1:

One-way ANOVA table testing the significance of the differences in water:sediment ratios (peat and floc combined) between treatments on individual sampling days

Table 4.1a:

One-way ANOVA table testing the significance of the differences in water:sediment ratios (peat and floc combined) between treatments on individual sampling days (***=p<0.001; ns= not significant)

		Sum of Squares	df	Mean Square	F
DAY7	Between Groups	151.952	3	50.651	1.080 ns
	Within Groups	2110.612	45	46.902	
	Total	2262.564	48		
DAY14	Between Groups	143.968	3	47.989	1.450 ns
	Within Groups	1489.607	45	33.102	
	Total	1633.576	48		
DAY21	Between Groups	72.255	3	24.085	1.294 ns
	Within Groups	837.422	45	18.609	
	Total	909.677	48		
DAY28	Between Groups	94.818	3	31.606	1.611 ns
	Within Groups	882.665	45	19.615	
	Total	977.483	48		
DAY35	Between Groups	79.885	3	26.628	1.247 ns
	Within Groups	960.690	45	21.349	
	Total	1040.575	48		
DAY49	Between Groups	536.642	3	178.881	.818***
	Within Groups	627.974	45	13.955	
	Total	1164.616	48		

Table 4.1b

Tukey's post hoc test for ANOVA table shown in Table 4.1a (Day 49 only; all other days had non-significant values) (**=p<0.01; ***=p<0.001)

		Mean Difference	Std. Error	95% Confidence Interval	
(I) Treatment	(J) Treatment			Lower Bound	Upper Bound
Continuously wet anaerobic	Dried/rewet anaerobic	5.59**	1.532	1.5025	9.6858
	Continuously wet aerated	3.00	1.532	-1.0912	7.0921
	Dried/rewet aerated	8.68***	1.532	4.5934	12.7767
Dried/rewet anaerobic	Dried/rewet aerated	3.09	1.532	-1.0008	7.1825
Continuously wet aerated	Dried/rewet anaerobic	2.59	1.532	-1.4979	6.6854
	Dried/rewet aerated	5.68**	1.532	1.5929	9.7763

APPENDIX 4.2:

One-way ANOVAs for peat on individual days per combination of treatment and incubation type

1. Anaerobic, difference between continuously wet and dried/rewet peat

1.1 pH (n=5):

Test of Homogeneity of Variances

	Levene Statistic	df1	df2	Sig.
PH1	.004	1	8	.950
PH7	.550	1	8	.479
PH14	.001	1	8	.974
PH21	.103	1	8	.756
PH28	.495	1	8	.502
PH35	.164	1	8	.696
PH49	.218	1	8	.653

ANOVA

		Sum of Squares	df	Mean Square	F	Sig.
PH1	Between Groups	.471	1	.471	17.773	.003
	Within Groups	.212	8	.026		
	Total	.683	9			
PH7	Between Groups	.199	1	.199	6.986	.030
	Within Groups	.228	8	.028		
	Total	.426	9			
PH14	Between Groups	.114	1	.114	2.463	.155
	Within Groups	.372	8	.046		
	Total	.486	9			
PH21	Between Groups	.002	1	.002	.042	.843
	Within Groups	.430	8	.054		
	Total	.432	9			
PH28	Between Groups	.016	1	.016	.465	.514
	Within Groups	.275	8	.034		
	Total	.291	9			
PH35	Between Groups	.001	1	.001	.011	.917
	Within Groups	.448	8	.056		
	Total	.448	9			
PH49	Between Groups	.000	1	.000	.000	1.000
	Within Groups	.398	8	.050		
	Total	.398	9			

1.2 EC, Kruskall-Wallis (n=6)

Ranks

	Treatment	N	Mean Rank
EC1	1	12	11.67
	2	12	13.33
	Total	24	
EC7	1	12	10.96
	2	12	14.04
	Total	24	
EC14	1	12	11.04
	2	12	13.96
	Total	24	
EC21	1	12	10.92
	2	12	14.08
	Total	24	
EC28	1	12	11.00
	2	12	14.00
	Total	24	
EC35	1	12	11.00
	2	12	14.00
	Total	24	
EC49	1	12	11.00
	2	12	14.00
	Total	24	

Test Statistics[a,b]

	EC1	EC7	EC14	EC21	EC28	EC35	EC49
Chi-Square	.333	1.141	1.021	1.204	1.080	1.080	1.080
df	1	1	1	1	1	1	1
Asymp. Sig.	.564	.285	.312	.273	.299	.299	.299

a. Kruskal Wallis Test

b. Grouping Variable: Treatment

1.3 Iron, one-way ANOVA, n=5

Test of Homogeneity of Variances

	Levene Statistic	df1	df2	Sig.
FE7	.071	1	18	.792
FE21	.942	1	18	.345
FE35	.331	1	18	.572
FE49	.035	1	18	.854

ANOVA

		Sum of Squares	df	Mean Square	F	Sig.
FE7	Between Groups	1.290	1	1.290	.352	.560
	Within Groups	65.896	18	3.661		
	Total	67.186	19			
FE21	Between Groups	5.682	1	5.682	1.697	.209
	Within Groups	60.256	18	3.348		
	Total	65.938	19			
FE35	Between Groups	4.532	1	4.532	.754	.397
	Within Groups	108.152	18	6.008		
	Total	112.684	19			
FE49	Between Groups	.468	1	.468	.150	.703
	Within Groups	55.963	18	3.109		
	Total	56.431	19			

1.4 Calcium, log-transformed, on-way ANOVA, n=6

Test of Homogeneity of Variances

	Levene Statistic	df1	df2	Sig.
TRANFE49	.019	1	10	.894
LG10CA7	2.627	1	10	.136
LG10CA21	.497	1	10	.497
LG10CA35	.107	1	10	.751
LG10CA49	1.557	1	10	.241

ANOVA

		Sum of Squares	df	Mean Square	F	Sig.
TRANFE49	Between Groups	.006	1	.006	.091	.769
	Within Groups	.695	10	.070		
	Total	.701	11			
LG10CA7	Between Groups	.012	1	.012	.569	.468
	Within Groups	.205	10	.020		
	Total	.217	11			
LG10CA21	Between Groups	.003	1	.003	.241	.634
	Within Groups	.132	10	.013		
	Total	.135	11			
LG10CA35	Between Groups	.000	1	.000	.010	.922
	Within Groups	.138	10	.014		
	Total	.138	11			
LG10CA49	Between Groups	.001	1	.001	.097	.762
	Within Groups	.146	10	.015		
	Total	.147	11			

1.5 TFP, log-transformed, one-way ANOVA, n=6

Test of Homogeneity of Variances

	Levene Statistic	df1	df2	Sig.
LG10P7	.000	1	10	.986
LG10P21	2.986	1	10	.115
LG10P35	.662	1	10	.435
LG10P49	2.092	1	10	.179

ANOVA

		Sum of Squares	df	Mean Square	F	Sig.
LG10P7	Between Groups	.173	1	.173	1.296	.281
	Within Groups	1.335	10	.133		
	Total	1.508	11			
LG10P21	Between Groups	.129	1	.129	2.739	.129
	Within Groups	.473	10	.047		
	Total	.602	11			
LG10P35	Between Groups	.088	1	.088	.769	.401
	Within Groups	1.146	10	.115		
	Total	1.234	11			
LG10P49	Between Groups	.076	1	.076	1.150	.309
	Within Groups	.659	10	.066		
	Total	.735	11			

1.6 Sulfate, one-way ANOVA, n=6

Test of Homogeneity of Variances

	Levene Statistic	df1	df2	Sig.
SULF7	.087	1	22	.771
SULF21	.123	1	22	.729
SULF35	.778	1	22	.387
SULF49	2.360	1	22	.139

ANOVA

		Sum of Squares	df	Mean Square	F	Sig.
SULF7	Between Groups	1176.000	1	1176.000	8.812	.007
	Within Groups	2935.833	22	133.447		
	Total	4111.833	23			
SULF21	Between Groups	18.375	1	18.375	.064	.803
	Within Groups	6311.250	22	286.875		
	Total	6329.625	23			
SULF35	Between Groups	748.167	1	748.167	1.461	.240
	Within Groups	11265.167	22	512.053		
	Total	12013.333	23			
SULF49	Between Groups	937.500	1	937.500	2.161	.156
	Within Groups	9546.333	22	433.924		
	Total	10483.833	23			

2 Aerated, difference between continuously wet and dried/rewet peat

2.1 pH, Kurskall-Wallis, n=5

Ranks

	Treatment	N	Mean Rank
PH1	1	10	15.45
	2	10	5.55
	Total	20	
PH7	1	10	15.45
	2	10	5.55
	Total	20	
PH14	1	10	14.80
	2	10	6.20
	Total	20	
PH21	1	10	14.10
	2	10	6.90
	Total	20	
PH28	1	10	14.50
	2	10	6.50
	Total	20	
PH35	1	10	13.90
	2	10	7.10
	Total	20	
PH49	1	10	12.25
	2	10	8.75
	Total	20	

2.2 EC, Kruskall-Wallis, n=6

Test Statistics[a,b]

	PH1	PH7	PH14	PH21	PH28	PH35	PH49
Chi-Square	14.023	14.033	10.606	7.411	9.150	6.616	1.755
df	1	1	1	1	1	1	1
Asymp. Sig.	.000	.000	.001	.006	.002	.010	.185

a. Kruskal Wallis Test

b. Grouping Variable: Treatment

Ranks

	Treatment	N	Mean Rank
EC1	1	12	12.25
	2	12	12.75
	Total	24	
EC7	1	12	11.58
	2	12	13.42
	Total	24	
EC14	1	12	12.33
	2	12	12.67
	Total	24	
EC21	1	12	12.50
	2	12	12.50
	Total	24	
EC28	1	12	12.79
	2	12	12.21
	Total	24	
EC35	1	12	12.58
	2	12	12.42
	Total	24	
EC49	1	12	12.67
	2	12	12.33
	Total	24	

Test Statistics[a,b]

	EC1	EC7	EC14	EC21	EC28	EC35	EC49
Chi-Square	.030	.403	.013	.000	.041	.003	.013
df	1	1	1	1	1	1	1
Asymp. Sig.	.862	.525	.908	1.000	.840	.954	.908

a. Kruskal Wallis Test

b. Grouping Variable: Treatment

2.3 Iron, one-way ANOVA, n=5

Test of Homogeneity of Variances

	Levene Statistic	df1	df2	Sig.
FE7	1.080	1	18	.312
FE21	8.440	1	18	.009
FE35	.996	1	18	.331
FE49	.655	1	18	.429

ANOVA

		Sum of Squares	df	Mean Square	F	Sig.
FE7	Between Groups	.003	1	.003	.006	.941
	Within Groups	9.216	18	.512		
	Total	9.219	19			
FE21	Between Groups	.937	1	.937	1.260	.276
	Within Groups	13.387	18	.744		
	Total	14.324	19			
FE35	Between Groups	.202	1	.202	1.187	.290
	Within Groups	3.062	18	.170		
	Total	3.264	19			
FE49	Between Groups	.051	1	.051	1.182	.291
	Within Groups	.777	18	.043		
	Total	.828	19			

2.4 Calcium, one-way ANOVA, n=6

Test of Homogeneity of Variances

	Levene Statistic	df1	df2	Sig.
LG10CA7	.297	1	10	.598
LG10CA21	.933	1	10	.357
LG10CA35	.016	1	10	.901
LG10CA49	.654	1	10	.438

ANOVA

		Sum of Squares	df	Mean Square	F	Sig.
LG10CA7	Between Groups	.095	1	.095	14.549	.003
	Within Groups	.065	10	.007		
	Total	.160	11			
LG10CA21	Between Groups	.468	1	.468	28.180	.000
	Within Groups	.166	10	.017		
	Total	.634	11			
LG10CA35	Between Groups	.327	1	.327	14.947	.003
	Within Groups	.219	10	.022		
	Total	.545	11			
LG10CA49	Between Groups	.292	1	.292	12.924	.005
	Within Groups	.226	10	.023		
	Total	.518	11			

2.5 TFP, log-transformed, one-way ANOVA, n=6

Test of Homogeneity of Variances

	Levene Statistic	df1	df2	Sig.
LG10P7	.212	1	10	.655
LG10P21	.181	1	10	.679
LG10P35	4.313	1	10	.065
LG10P49	1.867	1	10	.202

ANOVA

		Sum of Squares	df	Mean Square	F	Sig.
LG10P7	Between Groups	.009	1	.009	.089	.771
	Within Groups	1.000	10	.100		
	Total	1.009	11			
LG10P21	Between Groups	.007	1	.007	.041	.843
	Within Groups	1.737	10	.174		
	Total	1.744	11			
LG10P35	Between Groups	.088	1	.088	1.770	.213
	Within Groups	.495	10	.049		
	Total	.582	11			
LG10P49	Between Groups	.143	1	.143	3.170	.105
	Within Groups	.452	10	.045		
	Total	.596	11			

2.6 Sulfate, log-transformed, one-way ANOVAs, n=6

Test of Homogeneity of Variances

	Levene Statistic	df1	df2	Sig.
LG10S7	1.671	1	10	.225
LG10S21	.154	1	10	.703
LG10S35	.082	1	10	.781
LG10S49	3.731	1	10	.082

ANOVA

		Sum of Squares	df	Mean Square	F	Sig.
LG10S7	Between Groups	.106	1	.106	5.356	.043
	Within Groups	.198	10	.020		
	Total	.304	11			
LG10S21	Between Groups	.458	1	.458	12.610	.005
	Within Groups	.364	10	.036		
	Total	.822	11			
LG10S35	Between Groups	.196	1	.196	14.136	.004
	Within Groups	.139	10	.014		
	Total	.335	11			
LG10S49	Between Groups	.144	1	.144	7.818	.019
	Within Groups	.185	10	.018		
	Total	.329	11			

3 Continuously wet, difference between anaerobic and aerated peat

3.1 pH, Kruskall-Wallis, n=5

Ranks

	Incubation type	N	Mean Rank
PH1	anaerobic	6	8.83
	aerobic	6	4.17
	Total	12	
PH7	anaerobic	6	8.75
	aerobic	6	4.25
	Total	12	
PH14	anaerobic	6	9.17
	aerobic	6	3.83
	Total	12	
PH21	anaerobic	6	9.17
	aerobic	6	3.83
	Total	12	
PH28	anaerobic	6	9.33
	aerobic	6	3.67
	Total	12	
PH35	anaerobic	6	9.33
	aerobic	6	3.67
	Total	12	
PH49	anaerobic	6	9.33
	aerobic	6	3.67
	Total	12	

Test Statistics[a,b]

	PH1	PH7	PH14	PH21	PH28	PH35	PH49
Chi-Square	5.026	4.689	6.564	6.564	7.410	7.410	7.436
df	1	1	1	1	1	1	1
Asymp. Sig.	.025	.030	.010	.010	.006	.006	.006

a. Kruskal Wallis Test

b. Grouping Variable: Incubation type

3.2 EC, log-transformed, one-way ANOVA, n=6

Test of Homogeneity of Variances

	Levene Statistic	df1	df2	Sig.
COMPUTE logec1 = LG10(ec1) (COMPUTE)	3.708	1	22	.067
COMPUTE logec7 = LG10(ec7) (COMPUTE)	3.481	1	22	.075
LOGEC14	4.103	1	22	.055
LOGEC21	9.063	1	22	.006
LOGEC35	7.820	1	22	.011
LOGEC28	8.988	1	22	.007
LOGEC49	.001	1	22	.972

ANOVA

		Sum of Squares	df	Mean Square	F	Sig.
COMPUTE logec1 = LG10(ec1) (COMPUTE)	Between Groups	.016	1	.016	.563	.461
	Within Groups	.640	22	.029		
	Total	.656	23			
COMPUTE logec7 = LG10(ec7) (COMPUTE)	Between Groups	.021	1	.021	.814	.377
	Within Groups	.577	22	.026		
	Total	.598	23			
LOGEC14	Between Groups	.054	1	.054	2.360	.139
	Within Groups	.507	22	.023		
	Total	.561	23			
LOGEC21	Between Groups	.140	1	.140	6.493	.018
	Within Groups	.473	22	.022		
	Total	.613	23			
LOGEC35	Between Groups	.214	1	.214	11.663	.002
	Within Groups	.404	22	.018		
	Total	.618	23			
LOGEC28	Between Groups	.176	1	.176	9.078	.006
	Within Groups	.427	22	.019		
	Total	.604	23			
LOGEC49	Between Groups	.452	1	.452	14.613	.001
	Within Groups	.681	22	.031		
	Total	1.134	23			

3.3 Iron, one-way ANOVAs, log-transformed, n=5

Test of Homogeneity of Variances

	Levene Statistic	df1	df2	Sig.
TRANSFE7	.236	1	8	.640
TRANFE21	1.433	1	8	.266
TRANFE35	6.140	1	8	.038
TRANFE49	6.309	1	8	.036

ANOVA

		Sum of Squares	df	Mean Square	F	Sig.
TRANSFE7	Between Groups	.112	1	.112	1.822	.214
	Within Groups	.493	8	.062		
	Total	.605	9			
TRANFE21	Between Groups	.001	1	.001	.017	.900
	Within Groups	.530	8	.066		
	Total	.531	9			
TRANFE35	Between Groups	.234	1	.234	3.524	.097
	Within Groups	.532	8	.066		
	Total	.766	9			
TRANFE49	Between Groups	.259	1	.259	6.199	.038
	Within Groups	.334	8	.042		
	Total	.593	9			

3.4 Calcium, log-transformed, 0ne-way ANOVAs, n=6

Test of Homogeneity of Variances

	Levene Statistic	df1	df2	Sig.
LG10CA7	3.942	1	10	.075
LG10CA21	.019	1	10	.892
LG10CA35	.143	1	10	.713
LG10CA49	.149	1	10	.708

ANOVA

		Sum of Squares	df	Mean Square	F	Sig.
LG10CA7	Between Groups	.252	1	.252	13.052	.005
	Within Groups	.193	10	.019		
	Total	.445	11			
LG10CA21	Between Groups	.882	1	.882	39.896	.000
	Within Groups	.221	10	.022		
	Total	1.103	11			
LG10CA35	Between Groups	1.276	1	1.276	62.956	.000
	Within Groups	.203	10	.020		
	Total	1.479	11			
LG10CA49	Between Groups	1.840	1	1.840	79.729	.000
	Within Groups	.231	10	.023		
	Total	2.070	11			

3.5 TFP, log-transformed, one-way ANOVAs, n=6

Test of Homogeneity of Variances

	Levene Statistic	df1	df2	Sig.
LG10P7	.098	1	10	.760
LG10P21	2.822	1	10	.124
LG10P35	2.234	1	10	.166
LG10P49	.691	1	10	.425

ANOVA

		Sum of Squares	df	Mean Square	F	Sig.
LG10P7	Between Groups	.014	1	.014	.129	.727
	Within Groups	1.083	10	.108		
	Total	1.097	11			
LG10P21	Between Groups	.702	1	.702	6.189	.032
	Within Groups	1.134	10	.113		
	Total	1.836	11			
LG10P35	Between Groups	.211	1	.211	4.598	.058
	Within Groups	.459	10	.046		
	Total	.670	11			
LG10P49	Between Groups	.361	1	.361	7.525	.021
	Within Groups	.479	10	.048		
	Total	.840	11			

3.6 Sulfate, log-transformed, one-way ANOVAs, n=6

Test of Homogeneity of Variances

	Levene Statistic	df1	df2	Sig.
LG10S7	.024	1	10	.880
LG10S21	.020	1	10	.890
LG10S35	.019	1	10	.893
LG10S49	.804	1	10	.391

ANOVA

		Sum of Squares	df	Mean Square	F	Sig.
LG10S7	Between Groups	1.164	1	1.164	35.008	.000
	Within Groups	.333	10	.033		
	Total	1.497	11			
LG10S21	Between Groups	1.677	1	1.677	72.079	.000
	Within Groups	.233	10	.023		
	Total	1.910	11			
LG10S35	Between Groups	1.284	1	1.284	101.260	.000
	Within Groups	.127	10	.013		
	Total	1.411	11			
LG10S49	Between Groups	2.081	1	2.081	92.263	.000
	Within Groups	.226	10	.023		
	Total	2.306	11			

4 Dried/rewet peat, difference between anaerobic and aerated

4.1 pH, Kruskall-Wallis, n=5

Ranks

	Incubation type	N	Mean Rank
PH1	anaerobic	6	6.83
	aerobic	6	6.17
	Total	12	
PH7	anaerobic	6	6.42
	aerobic	6	6.58
	Total	12	
PH14	anaerobic	6	7.00
	aerobic	6	6.00
	Total	12	
PH21	anaerobic	6	8.33
	aerobic	6	4.67
	Total	12	
PH28	anaerobic	6	8.67
	aerobic	6	4.33
	Total	12	
PH35	anaerobic	6	8.83
	aerobic	6	4.17
	Total	12	
PH49	anaerobic	6	9.50
	aerobic	6	3.50
	Total	12	

Test Statistics[a,b]

	PH1	PH7	PH14	PH21	PH28	PH35	PH49
Chi-Square	.103	.006	.232	3.124	4.333	5.026	8.337
df	1	1	1	1	1	1	1
Asymp. Sig.	.748	.936	.630	.077	.037	.025	.004

a. Kruskal Wallis Test

b. Grouping Variable: Incubation type

4.2 EC, Kruskall-Wallis, n=6

Ranks

	Incubation type	N	Mean Rank
EC1	1	12	12.92
	2	12	12.08
	Total	24	
EC7	1	12	12.83
	2	12	12.17
	Total	24	
EC14	1	12	13.58
	2	12	11.42
	Total	24	
EC21	1	12	12.67
	2	12	12.33
	Total	24	
EC28	1	12	12.67
	2	12	12.33
	Total	24	
EC35	1	12	12.50
	2	12	12.50
	Total	24	
EC49	1	12	12.50
	2	12	12.50
	Total	24	

Test Statistics[a,b]

	EC1	EC7	EC14	EC21	EC28	EC35	EC49
Chi-Square	.083	.053	.563	.013	.013	.000	.000
df	1	1	1	1	1	1	1
Asymp. Sig.	.773	.817	.453	.908	.908	1.000	1.000

a. Kruskal Wallis Test

b. Grouping Variable: Incubation type

4.3 Iron, log-transformed, one-way ANOVAs, n=5

Test of Homogeneity of Variances

	Levene Statistic	df1	df2	Sig.
TRANSFE7	5.901	1	8	.041
TRANFE21	3.517	1	8	.098
TRANFE35	3.231	1	8	.110
TRANFE49	2.631	1	8	.143

ANOVA

		Sum of Squares	df	Mean Square	F	Sig.
TRANSFE7	Between Groups	.091	1	.091	6.645	.033
	Within Groups	.109	8	.014		
	Total	.200	9			
TRANFE21	Between Groups	.015	1	.015	.234	.642
	Within Groups	.500	8	.062		
	Total	.515	9			
TRANFE35	Between Groups	.054	1	.054	.669	.437
	Within Groups	.640	8	.080		
	Total	.694	9			
TRANFE49	Between Groups	.191	1	.191	4.291	.072
	Within Groups	.356	8	.045		
	Total	.547	9			

4.4 Calcium, log-transformed, one-way ANOVAs, n=6

Test of Homogeneity of Variances

	Levene Statistic	df1	df2	Sig.
LG10CA7	1.060	1	10	.327
LG10CA21	.185	1	10	.676
LG10CA35	.402	1	10	.540
LG10CA49	.133	1	10	.723

ANOVA

		Sum of Squares	df	Mean Square	F	Sig.
LG10CA7	Between Groups	.007	1	.007	.945	.354
	Within Groups	.077	10	.008		
	Total	.085	11			
LG10CA21	Between Groups	.040	1	.040	5.178	.046
	Within Groups	.077	10	.008		
	Total	.116	11			
LG10CA35	Between Groups	.299	1	.299	19.451	.001
	Within Groups	.153	10	.015		
	Total	.452	11			
LG10CA49	Between Groups	.729	1	.729	51.803	.000
	Within Groups	.141	10	.014		
	Total	.869	11			

4.5 TFP, log-transformed, one-way ANOVAs, n=6

Test of Homogeneity of Variances

	Levene Statistic	df1	df2	Sig.
LG10P7	.006	1	10	.938
LG10P21	.037	1	10	.851
LG10P35	.358	1	10	.563
LG10P49	3.519	1	10	.090

ANOVA

		Sum of Squares	df	Mean Square	F	Sig.
LG10P7	Between Groups	.395	1	.395	3.156	.106
	Within Groups	1.252	10	.125		
	Total	1.647	11			
LG10P21	Between Groups	1.238	1	1.238	11.517	.007
	Within Groups	1.075	10	.108		
	Total	2.314	11			
LG10P35	Between Groups	1.107	1	1.107	9.370	.012
	Within Groups	1.182	10	.118		
	Total	2.289	11			
LG10P49	Between Groups	1.574	1	1.574	24.921	.001
	Within Groups	.632	10	.063		
	Total	2.206	11			

4.6 Sulfate, log-transformed, one-way ANOVAs, n=6

Test of Homogeneity of Variances

	Levene Statistic	df1	df2	Sig.
LG10S7	.056	1	10	.817
LG10S21	.083	1	10	.779
LG10S35	2.224	1	10	.167
LG10S49	6.745	1	10	.027

ANOVA

		Sum of Squares	df	Mean Square	F	Sig.
LG10S7	Between Groups	.096	1	.096	15.853	.003
	Within Groups	.061	10	.006		
	Total	.157	11			
LG10S21	Between Groups	.457	1	.457	10.302	.009
	Within Groups	.444	10	.044		
	Total	.901	11			
LG10S35	Between Groups	1.104	1	1.104	33.976	.000
	Within Groups	.325	10	.032		
	Total	1.429	11			
LG10S49	Between Groups	2.249	1	2.249	73.919	.000
	Within Groups	.304	10	.030		
	Total	2.554	11			

Appendix 4.3a:

Spearman's rank order correlations between dependent variables over time (n=4), and on individual sampling days (n=6, Sites 1-6) within the four treatment groups (wet anaerobic, dry anaerobic, wet aerated, dry aerated). For the correlations over time, for each of the treatment groups, the mean of each variable on the four sampling days was correlated with the mean of every other variable on the four sampling days. (* p<0.10; **p<0.05; ***p<0.01)

	Peat				Floc			
	wet anaerobic	dry anaerobic	wet air	dry air	wet anaerobic	dry anaerobic	wet air	dry air
ph-ec								
Temporal (n=4)	-0.86	0.13	-1.00***	-1.00***	0.84	0.56	-0.89	-0.45
Day 7 (n=6)	0.69	0.84**	0.10	0.10	0.81**	0.81**	0.71	0.08
Day 21(n=6)	0.78	0.75	-0.32	-0.29	0.71	0.67	0.83**	-0.49
Day 35(n=6)	0.80**	0.49	-0.56	-0.60	0.90***	-0.22	0.16	0.48
Day 49 (n=6)	0.48	0.34	-0.80**	-0.52	0.97***	-0.64	-0.97***	0.86**
pH-P								
Temporal	-0.93*	0.97**	0.60	0.94*	-0.66	-0.69	-0.29	-0.81
Day 7	0.36	0.71	0.67	0.39	0.05	-0.91***	-0.61	-0.96***
Day 21	0.46	0.76	0.97***	0.53	-0.47	-0.84**	-0.38	-0.74
Day 35	0.61	0.84**	0.94***	0.58	-0.72	-0.83**	0.89**	-0.10
Day 49	0.39	0.83**	0.54	0.14	-0.45	-0.96***	-0.99***	0.34
pH-Ca								
Temporal	-0.31	-0.86	-0.99***	-0.99***	0.00	-0.95**	-0.99***	-0.99***
Day 7	0.83**	0.86**	-0.79	-0.01	0.87**	0.97***	0.59	0.75
Day 21	0.95***	0.48	-0.36	-0.60	0.78	0.88**	0.64	0.45
Day 35	0.93***	0.13	-0.49	-0.85**	0.95***	0.90***	-0.49	0.33
Day 49	0.72	0.18	-0.59	-0.55	0.93***	0.68	-0.60	-0.42
pH-fe								
Temporal	0.86	0.93*	-0.49	-0.05	-0.84	-0.98**	-0.92*	-0.98**
Day 7	-0.25	-0.51	-0.03	0.03	-0.45	-0.77	-0.86**	-0.87**
Day 21	-0.62	-0.71	0.51	0.25	-0.19	-0.75	-0.93***	-0.88**
Day 35	-0.23	-0.82**	-0.67	0.21	-	-0.80**	-0.99***	-0.91***
Day 49	-0.02	-0.82**	-0.87**	-0.31	0.17	-0.95***	-1.00***	0.23
pH-SO4								
Temporal	-0.89	-0.93*	-0.96**	-0.99***	-0.90*	-0.70	-0.93*	0.34
Day 7	-0.15	-0.04	-0.29	-0.93***	0.18	0.62	0.40	0.53
Day 21	-0.29	-0.88**	-0.44	-0.42	0.79	-0.76	0.07	-0.15
Day 35	-0.22	-0.81	-0.71	-0.82**	0.79	0.24	-0.72	0.02
Day 49	-0.49	-0.95***	-0.66	-0.96***	0.75	0.23	-0.98***	-0.84**
pH-northings								
Day 7	-0.38	-0.48	-0.13	-0.35	0.14	0.28	0.50	0.25
Day 21	-0.48	-0.37	0.29	-0.48	0.35	0.26	0.38	0.21
Day 35	-0.34	-0.41	0.23	-0.60	0.31	0.31	0.09	-0.31
Day 49	-0.36	-0.44	0.20	-0.55	0.34	0.02	0.02	0.06
pH-eastings								
Day 7	0.08	0.04	-0.13	-0.09	-0.64	-0.77	-0.74	-0.69
Day 21	0.13	-0.11	-0.58	0.00	-0.69	-0.75	-0.69	-0.69
Day 35	0.02	-0.03	-0.54	0.16	-0.67	-0.78	-0.37	0.28
Day 49	0.04	-0.02	-0.41	0.09	-0.66	-0.46	-0.29	0.30
ec-P								
Temporal	0.94*	0.34	-0.63	-0.94*	-0.79	-0.72	0.66	0.77
Day 7	0.66	0.66	0.00	0.69	-0.02	-0.85**	-0.27	-0.21
Day 21	0.70	0.87**	-0.37	0.03	-0.13	-0.78	-0.28	0.56
Day 35	0.46	0.75	-0.28	-0.68	-0.65	0.50	0.10	0.69
Day 49	0.62	0.68	-0.26	0.48	-0.44	0.59	0.98***	0.74
ec-Ca								
Temporal	0.47	0.38	0.99***	1.00***	0.14	-0.34	0.88	0.58
Day 7	0.96***	0.61	0.22	-0.80**	0.98***	0.92***	0.93***	0.42
Day 21	0.92***	0.03	0.90***	0.19	0.99***	0.82**	0.72	0.40
Day 35	0.91***	0.27	0.85**	0.78	0.99***	-0.24	0.76	-0.09
Day 49	0.92***	0.39	0.82**	0.75	0.98***	0.04	0.78	-0.82**

	Peat				Floc			
	wet anaerobic	dry anaerobic	wet air	dry air	wet anaerobic	dry anaerobic	wet air	dry air
ec-Fe								
Temporal	-0.63	-0.17	0.53	0.04	-0.78	-0.42	0.99***	0.40
Day 7	-0.63	-0.42	-0.84**	-0.87**	-0.78	-0.88**	-0.68	-0.38
Day 21	-0.83**	-0.93***	-0.82**	-0.71	-0.51	-0.52	-0.78	0.39
Day 35	-0.71	-0.55	0.06	-0.68	-	0.62	-0.03	-0.12
Day 49	-0.70	-0.43	0.59	-0.35	0.04	0.81**	0.98***	0.29
ec-So4								
Temporal	0.96**	0.16	0.96**	0.98**	-0.67	-0.91*	0.99***	-0.96**
Day 7	0.20	-0.10	0.65	-0.39	0.30	0.96***	0.83**	-0.17
Day 21	-0.12	-0.88**	0.93***	0.45	0.96***	-0.59	0.39	0.45
Day 35	-0.10	-0.22	0.78	0.94***	0.64	-0.16	0.58	-0.82**
Day 49	0.11	-0.17	0.89**	0.71	0.67	0.56	0.98***	-0.90***
ec-northings								
Day 7	-0.58	-0.63	-0.91***	-0.69	-0.09	0.20	-0.09	-0.16
Day 21	-0.63	-0.67	-0.92***	-0.49	-0.10	0.49	-0.13	-0.13
Day 35	-0.59	-0.85**	-0.87**	0.11	0.00	-0.05	0.30	-0.10
Day 49	-0.47	-0.85**	-0.65	0.12	0.30	0.27	0.11	-0.25
ec-eastings								
Day 7	0.45	0.26	0.78	0.67	-0.27	-0.61	-0.46	0.03
Day 21	0.53	0.41	0.87	0.67	-0.29	-0.73	-0.39	0.22
Day 35	0.35	0.74	0.86	0.23	-0.35	0.12	-0.72	0.52
Day 49	0.37	0.84	0.60	0.23	-0.67	-0.10	0.07	0.70
P-Ca								
Temporal	0.59	-0.73	-0.53	-0.91*	0.47	0.69	0.23	0.89
Day 7	0.60	0.50	-0.73	-0.19	-0.02	-0.93***	-0.41	-0.83**
Day 21	0.68	0.40	-0.41	-0.46	-0.14	-0.96***	0.40	-0.46
Day 35	0.62	0.36	-0.29	-0.73	-0.73	-0.95***	-0.51	-0.73
Day 49	0.76	0.36	-0.16	0.50	-0.29	-0.75	0.65	-0.96***
P-Fe								
Temporal	-0.64	0.81	-0.40	-0.38	0.94*	0.67	0.63	0.84
Day 7	-0.37	-0.84**	0.27	-0.65	0.03	0.77	0.18	0.88**
Day 21	-0.29	-0.69	0.56	-0.28	0.44	0.78	0.30	0.62
Day 35	0.16	-0.65	-0.73	0.14	-	0.96***	-0.92***	0.42
Day 49	0.04	-0.68	-0.62	-0.41	-0.69	0.92***	0.99***	0.42
P-SO4								
Temporal	0.99***	-0.87	-0.49	-0.90*	0.77	0.94*	0.59	-0.60
Day 7	-0.28	-0.39	0.14	-0.68	0.08	-0.72	-0.44	-0.30
Day 21	0.59	-0.69	-0.49	-0.01	-0.01	0.38	0.74	0.77
Day 35	0.56	-0.56	-0.56	-0.69	-0.92***	-0.32	-0.67	-0.62
Day 49	0.53	-0.75	-0.32	-0.01	-0.03	-0.29	0.98***	-0.73
P-northings								
Day 7	-0.86	-0.66	0.13	-0.75	-0.37	-0.58	-0.88**	-0.46
Day 21	-0.10	-0.57	0.29	-0.60	-0.30	-0.63	-0.08	-0.68
Day 35	-0.14	-0.585	-0.09	-0.48	-0.09	-0.36	-0.36	-0.30
Day 49	0.24	-0.64	0.02	0.35	-0.77	-0.28	0.11	-0.34
P-eastings								
Day 7	0.83	0.60	0.03	0.78	0.11	0.914	0.97***	0.81**
Day 21	0.24	0.41	-0.67	0.62	0.14	0.94***	-0.09	0.91***
Day 35	0.30	0.32	-0.34	0.39	0.51	0.73	-0.02	0.78
Day 49	-0.08	0.38	-0.59	-0.48	0.55	0.65	0.18	0.80**
Ca-Fe								
Temporal	0.22	-0.92*	0.51	-0.03	0.47	0.99***	0.90*	0.97**
Day 7	-0.45	-0.14	-0.10	0.64	-0.69	-0.86**	-0.51	-0.67
Day 21	-0.67	0.20	-0.59	-0.49	-0.45	-0.89**	-0.68	-0.54
Day 35	-0.42	0.36	-0.23	-0.57	-	-0.85**	0.59	-0.49
Day 49	-0.39	0.30	0.17	-0.55	-0.14	-0.45	0.64	-0.46

	Peat				Floc			
	wet anaerobic	dry anaerobic	wet air	dry air	wet anaerobic	dry anaerobic	wet air	dry air
Ca-SO4								
Temporal	0.64	0.96**	0.97**	0.98**	0.43	0.59	0.92*	-0.46
Day 7	0.10	0.37	0.49	0.17	0.14	0.78	0.96***	0.19
Day 21	-0.10	-0.10	0.98***	0.84**	0.97***	-0.54	0.81**	-0.20
Day 35	-0.15	0.40	0.95***	0.92***	0.74	0.17	0.93***	0.00
Day 49	0.09	0.12	0.85**	0.71	0.64	0.83**	0.65	0.75
Ca-northings								
Day 7	-0.52	-0.04	-0.36	0.51	0.07	0.26	0.04	0.40
Day 21	-0.48	0.11	-0.69	0.36	0.03	0.41	0.03	0.39
Day 35	-0.60	0.10	-0.70	0.58	0.06	0.41	0.27	0.52
Day 49	-0.41	-0.01	-0.69	0.62	0.20	0.52	0.31	0.40
Ca-eastings								
Day 7	0.42	-0.37	0.38	-0.37	-0.46	-0.75	-0.57	-0.78
Day 21	0.28	-0.33	0.79	0.03	-0.43	-0.81**	-0.57	-0.67
Day 35	0.38	-0.23	0.85**	-0.09	-0.46	-0.84**	-0.46	-0.73
Day 49	0.33	-0.06	0.65	-0.17	-0.63	-0.88**	-0.46	-0.83**
Fe-SO4								
Temporal	-0.57	-0.89	0.68	-0.05	0.94*	0.62	1.00***	-0.25
Day 7	-0.06	0.79	-0.25	0.29	-0.65	-0.79	-0.26	-0.23
Day 21	0.57	0.86**	-0.63	0.87**	-0.36	0.40	-0.16	0.11
Day 35	0.29	0.90**	0.01	-0.62	-	-0.44	0.80**	-0.34
Day 49	0.14	0.87**	0.38	0.06	0.24	0.06	0.99***	-0.58
Fe-northings								
Day 7	0.58	0.84**	0.70	0.43	0.05	-0.11	-0.18	-0.13
Day 21	0.83**	0.72	0.82	0.18	0.01	-0.10	-0.20	-0.20
Day 35	0.69	0.68	0.25	0.16	-	-0.14	0.03	0.21
Day 49	0.61	0.70	0.05	0.05	0.74	0.04	0.03	0.20
Fe-eastings								
Day 7	-0.21	-0.80**	-0.50	-0.66	-0.01	0.46	0.35	0.44
Day 21	-0.55	-0.41	-0.79	-0.59	-0.22	0.52	0.50	0.57
Day 35	-0.42	-0.35	-0.11	-0.61	-	0.54	0.23	-0.04
Day 49	-0.36	-0.34	0.21	-0.22	-0.46	0.31	0.23	0.03
SO4-northings								
Day 7	0.58	0.84**	-0.54	0.59	-0.40	0.16	0.02	-0.45
Day 21	0.57	0.36	-0.78	0.10	-0.04	0.15	-0.35	-0.70
Day 35	0.34	0.45	-0.54	0.32	0.07	-0.02	0.14	-0.36
Day 49	0.34	0.40	-0.87**	0.49	0.19	0.53	0.02	-0.02
SO4-eastings								
Day 7	-0.44	-0.84**	0.67	-0.27	0.39	-0.48	-0.56	-0.10
Day 21	-0.12	0.05	0.87***	0.36	-0.42	0.29	-0.17	0.61
Day 35	0.18	-0.04	0.79	0.13	-0.57	0.54	-0.20	-0.12
Day 49	0.21	0.04	0.85**	0.03	-0.61	-0.70	0.15	-0.48

Appendix 4.3b:

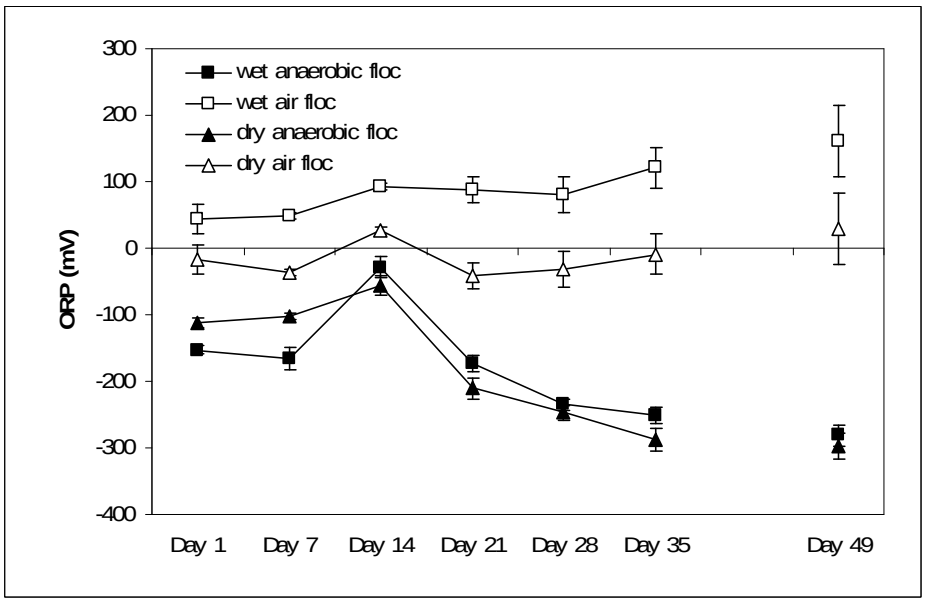
Spearman's rank order correlations between dependent variables over time (n=4), and on individual sampling days (n=5, Sites 1-5) within the four treatment groups (wet anaerobic, dry anaerobic, wet aerated, dry aerated). For the correlations over time, for each of the treatment groups, the mean of each variable on the four sampling days was correlated with the mean of every other variable on the four sampling days. (* p<0.10; **p<0.05; ***p<0.01)

	Peat				Floc			
	wet anaerobic	dry anaerobic	wet air	dry air	wet anaerobic	dry anaerobic	wet air	dry air
ph-ec								
Temporal	-0.51	0.10	-1.00***	-0.99***	0.78	0.45	0.77	-0.80
Day 7	0.81	0.97***	0.32	0.75	0.55	0.78	0.25	-0.53
Day 21	0.86	0.80	-0.55	0.26	0.62	0.65	0.49	-0.67
Day 35	0.98***	0.31	-0.61	-0.33	0.69	0.07	0.82	0.93**
Day 49	0.73	0.20	-0.72	-0.46	0.94**	0.43	0.77	0.86
pH-P								
Temporal	-0.68	0.98**	0.69	0.96**	-0.67	-0.69	-0.42	-0.90*
Day 7	0.70	0.56	0.36	0.35	-0.10	-0.88**	-0.95***	-0.91**
Day 21	0.19	0.54	0.93**	0.47	-0.39	-0.83	0.05	0.85
Day 35	0.10	0.74	0.72	0.56	-0.27	-0.94**	-0.33	0.55
Day 49	-0.06	0.72	-0.02	-0.37	-0.69	-0.84	0.31	0.35
pH-Ca								
Temporal	0.08	-0.35	-1.00***	-0.99***	0.07	-0.96**	0.04	-0.99***
Day 7	0.84	0.71	-0.79	-0.98***	0.72	0.99***	0.27	0.65
Day 21	0.88**	-0.66	-0.70	-0.87	0.76	0.92**	0.45	0.24
Day 35	0.93**	-0.88**	-0.86	-0.88**	0.84	0.91**	0.75	0.05
Day 49	0.68	-0.85	-0.93**	-0.90**	0.80	0.87	0.84	-0.42
pH-fe								
Temporal	0.79	0.89	0.57	-0.16	-0.86	-1.00***	-0.06	-0.96**
Day 7	-0.74	-0.38	-0.64	-0.51	0.78	-0.89**	-0.60	-0.86
Day 21	-0.99***	-0.92**	0.28	0.22	0.16	-0.97***	-0.75	-0.84
Day 35	-0.97***	-0.95***	0.90**	0.23	-	-0.96***	0.79	-0.96***
Day 49	-0.86	-0.97***	0.79	0.46	0.68	-0.99***	0.21	0.21
pH-SO4								
Temporal	-0.68	-0.86	-0.96**	-0.99***	-0.90*	-0.67	0.50	0.59
Day 7	-0.35	-0.14	-0.38	-0.89**	-0.32	0.42	0.25	0.60
Day 21	-0.64	-0.94**	-0.78	-0.63	0.69	-0.82	0.08	-0.57
Day 35	-0.19	-0.99***	-0.93**	-0.67	0.51	0.14	0.76	-0.65
Day 49	-0.29	-0.98***	-0.72	-0.94**	0.67	0.83	0.31	-0.95***
ec-P								
Temporal	0.97**	0.27	-0.75	-0.95**	-0.75	-0.69	-0.76	0.93*
Day 7	0.70	0.65	0.09	0.87	-0.42	-0.78	-0.37	0.33
Day 21	0.63	0.93**	0.93**	0.27	0.27	-0.79	0.17	0.57
Day 35	0.21	0.69	0.03	-0.65	0.02	-0.12	0.19	0.68
Day 49	0.59	0.65	0.18	0.72	-0.62	-0.58	0.28	0.77
ec-Ca								
Temporal	0.25	0.89	0.99***	0.99***	0.35	-0.26	0.66	0.87
Day 7	0.98***	0.76	0.19	-0.76	0.91**	0.87	0.94**	0.20
Day 21	1.00***	-0.67	0.90**	0.22	0.95***	0.88**	0.60	0.41
Day 35	0.92**	-0.20	0.87	0.71	0.96***	0.32	0.96**	0.06
Day 49	0.97***	0.27	0.90**	0.79	0.95***	0.62	0.97***	-0.82
ec-Fe								
Temporal	0.04	-0.30	-0.50	0.13	-0.77	-0.37	-0.31	0.63
Day 7	-0.73	-0.38	-0.87	-0.84	0.31	-0.65	0.40	0.52
Day 21	-0.88**	-0.95***	-0.94**	-0.77	-	-0.63	-0.20	0.74
Day 35	-0.94***	-0.56	-0.71	-0.76	-	0.07	0.57	-0.87
Day 49	-0.83	-0.43	-0.56	-0.79	0.40	-0.37	0.62	0.16
ec-So4								
Temporal	0.98**	0.37	0.95**	0.99***	-0.57	-0.83	0.94*	-0.94*
Day 7	0.22	-0.12	0.65	-0.95***	-0.48	0.90**	0.95**	-0.31
Day 21	-0.16	-0.86	0.93**	0.55	0.98***	-0.63	0.58	0.46
Day 35	-0.03	-0.22	0.75	0.92**	0.04	0.10	0.99***	-0.84
Day 49	0.25	-0.06	0.88**	0.71	0.52	0.78	0.28	-0.95***

	Peat				Floc			
	wet anaerobic	dry anaerobic	wet air	dry air	wet anaerobic	dry anaerobic	wet air	dry air
P-Ca								
Temporal	0.29	-0.18	-0.63	-0.92*	0.35	0.69	-0.76	0.94*
Day 7	0.70	0.13	-0.63	-0.41	-0.34	-0.90**	-0.47	-0.78
Day 21	0.59	-0.64	-0.79	-0.47	0.22	-0.95***	0.85	-0.48
Day 35	0.31	-0.52	-0.43	-0.70	-0.22	-0.96***	0.11	-0.63
Day 49	0.69	-0.42	-0.53	0.56	-0.42	-1.00***	0.18	-0.96***
P-Fe								
Temporal	-0.14	0.82	-0.14	-0.43	0.94*	0.67	0.85	0.82
Day 7	-0.38	-0.81	0.04	-0.83	0.50	0.74	0.58	0.85
Day 21	-0.27	-0.82	0.36	-0.34	0.36	0.76	-0.51	0.89**
Day 35	0.07	-0.78	0.65	0.12	-	0.89**	0.13	-0.47
Day 49	-0.10	-0.80	0.19	-0.18	-0.74	0.78	0.68	-0.10
P-SO4								
Temporal	0.99***	-0.74	-0.57	-0.93*	0.77	0.98**	-0.81	-0.75
Day 7	-0.28	-0.52	0.25	-0.72	-0.01	-0.52	-0.45	-0.26
Day 21	0.63	-0.63	-0.86	-0.02	0.30	0.48	0.87	0.90**
Day 35	0.86	-0.72	-0.60	-0.68	-0.83	-0.12	0.30	-0.35
Day 49	0.88**	-0.70	-0.10	0.45	0.00	-0.92**	-0.16	-0.58
Ca-Fe								
Temporal	0.55	-0.66	-0.62	0.04	0.29	0.98**	-0.51	0.92*
Day 7	-0.61	0.31	0.11	0.55	0.55	-0.85	0.18	-0.72
Day 21	-0.90**	0.77	-0.72	-0.49	0.11	-0.89**	-0.71	-0.30
Day 35	-0.82	0.85	-0.90**	-0.59	-0.83	-0.79	0.35	-0.19
Day 49	-0.70	0.72	-0.72	-0.73	0.13	-0.81	0.43	-0.15
Ca-SO4								
Temporal	0.19	0.74	0.97**	0.99***	0.38	0.61	0.88	-0.68
Day 7	0.13	0.50	0.52	0.92**	-0.72	0.57	1.00***	0.13
Day 21	-0.22	0.67	0.98***	0.84	0.99***	-0.73	0.92**	-0.52
Day 35	-0.05	0.80	0.97***	0.93**	0.32	-0.04	0.95***	-0.43
Day 49	0.44	0.91**	0.86	0.99***	0.46	0.95**	0.90**	0.65
Fe-SO4								
Temporal	-0.17	-0.88	-0.56	0.08	0.93*	0.64	-0.39	-0.35
Day 7	-0.06	0.89**	-0.23	0.80	-0.50	-0.31	0.22	-0.22
Day 21	0.58	0.89**	-0.75	-0.88**	0.15	0.87	-0.39	0.83
Day 35	0.32	0.90**	-0.91**	-0.76	-	-0.35	0.53	0.60
Day 49	0.31	0.91**	-0.83	-0.72	0.46	-0.76	0.26	-0.28

Appendix 4.4:

ORP in the floc incubations. Error bars are standard errors (n=6).



APPENDIX 4.5:

One-way ANOVAs for floc on individual days per combination of treatment and incubation type (all n=5)

1. Anaerobic, difference between continuously wet and dried/rewet floc

1.1 Kruskall-Wallis test, pH (n=5):

Ranks

	Treatment	N	Mean Rank
PH1	1	5	8.00
	2	5	3.00
	Total	10	
PH7	1	5	8.00
	2	5	3.00
	Total	10	
PH14	1	5	8.00
	2	5	3.00
	Total	10	
PH21	1	5	8.00
	2	5	3.00
	Total	10	
PH28	1	5	8.00
	2	5	3.00
	Total	10	
PH35	1	5	8.00
	2	5	3.00
	Total	10	
PH49	1	5	6.60
	2	5	4.40
	Total	10	

Test Statistics[a,b]

	PH1	PH7	PH14	PH21	PH28	PH35	PH49
Chi-Square	6.818	6.902	6.818	6.818	6.818	6.818	1.328
df	1	1	1	1	1	1	1
Asymp. Sig.	.009	.009	.009	.009	.009	.009	.249

a. Kruskal Wallis Test

b. Grouping Variable: Treatment

1.2a EC, log-transformed, one-way ANOVAs

Test of Homogeneity of Variances

	Levene Statistic	df1	df2	Sig.
LGEC7	.028	1	8	.870
LGEC21	1.652	1	8	.235
LGEC35	11.826	1	8	.009
LGEC49	14.526	1	8	.005
LNEC7	.028	1	8	.870
LNEC21	1.652	1	8	.235
LNEC35	11.826	1	8	.009
LNEC49	14.526	1	8	.005

ANOVA

		Sum of Squares	df	Mean Square	F	Sig.
LGEC7	Between Groups	.463	1	.463	349.790	.000
	Within Groups	.011	8	.001		
	Total	.474	9			
LGEC21	Between Groups	.476	1	.476	486.673	.000
	Within Groups	.008	8	.001		
	Total	.484	9			
LGEC35	Between Groups	.623	1	.623	615.224	.000
	Within Groups	.008	8	.001		
	Total	.632	9			
LGEC49	Between Groups	.607	1	.607	366.109	.000
	Within Groups	.013	8	.002		
	Total	.621	9			
LNEC7	Between Groups	2.456	1	2.456	349.790	.000
	Within Groups	.056	8	.007		
	Total	2.512	9			
LNEC21	Between Groups	2.526	1	2.526	486.673	.000
	Within Groups	.042	8	.005		
	Total	2.567	9			
LNEC35	Between Groups	3.305	1	3.305	615.224	.000
	Within Groups	.043	8	.005		
	Total	3.348	9			
LNEC49	Between Groups	3.220	1	3.220	366.109	.000
	Within Groups	.070	8	.009		
	Total	3.290	9			

1.2b EC, Kruskall-Wallis

Ranks

	Treatment	N	Mean Rank
EC1	1	5	3.00
	2	5	8.00
	Total	10	
EC7	1	5	3.00
	2	5	8.00
	Total	10	
EC14	1	5	3.00
	2	5	8.00
	Total	10	
EC21	1	5	3.00
	2	5	8.00
	Total	10	
EC28	1	5	3.00
	2	5	8.00
	Total	10	
EC35	1	5	3.00
	2	5	8.00
	Total	10	
EC49	1	5	3.00
	2	5	8.00
	Total	10	

Test Statistics[a,b]

	EC1	EC7	EC14	EC21	EC28	EC35	EC49
Chi-Square	6.818	6.818	6.818	6.818	6.818	6.818	6.818
df	1	1	1	1	1	1	1
Asymp. Sig.	.009	.009	.009	.009	.009	.009	.009

a. Kruskal Wallis Test

b. Grouping Variable: Treatment

1.3 Iron, Kruskall-Wallis

Ranks

	Treatment	N	Mean Rank
FE7	1	5	3.00
	2	5	8.00
	Total	10	
FE21	1	5	3.00
	2	5	8.00
	Total	10	
FE35	1	5	3.50
	2	5	7.50
	Total	10	
FE49	1	5	4.00
	2	5	7.00
	Total	10	

Test Statistics[a,b]

	FE7	FE21	FE35	FE49
Chi-Square	6.860	7.258	5.538	2.455
df	1	1	1	1
Asymp. Sig.	.009	.007	.019	.117

a. Kruskal Wallis Test

b. Grouping Variable: Treatment

1.4 Ca, Kruskall-Wallis

Ranks

	Treatment	N	Mean Rank
CA7	1	5	3.00
	2	5	8.00
	Total	10	
CA21	1	5	3.00
	2	5	8.00
	Total	10	
CA35	1	5	3.00
	2	5	8.00
	Total	10	
CA49	1	5	3.00
	2	5	8.00
	Total	10	

Test Statistics[a,b]

	CA7	CA21	CA35	CA49
Chi-Square	6.818	6.818	6.818	6.818
df	1	1	1	1
Asymp. Sig.	.009	.009	.009	.009

a. Kruskal Wallis Test

b. Grouping Variable: Treatment

1.5 TFP, log-transformed, one-way ANOVAs

Test of Homogeneity of Variances

	Levene Statistic	df1	df2	Sig.
LGP7	.093	1	8	.768
LGP21	2.123	1	8	.183
LGP35	.040	1	8	.847
LGP49	.816	1	8	.393

ANOVA

		Sum of Squares	df	Mean Square	F	Sig.
LGP7	Between Groups	16.472	1	16.472	910.473	.000
	Within Groups	.145	8	.018		
	Total	16.616	9			
LGP21	Between Groups	17.493	1	17.493	420.311	.000
	Within Groups	.333	8	.042		
	Total	17.826	9			
LGP35	Between Groups	22.089	1	22.089	745.099	.000
	Within Groups	.237	8	.030		
	Total	22.327	9			
LGP49	Between Groups	14.548	1	14.548	1361.463	.000
	Within Groups	.085	8	.011		
	Total	14.634	9			

1.6 Sulfate, Kruskall-Wallis

Ranks

	Treatment	N	Mean Rank
SULF7	1	5	3.80
	2	5	7.20
	Total	10	
SULF21	1	5	5.00
	2	5	6.00
	Total	10	
SULF35	1	5	8.00
	2	5	3.00
	Total	10	
SULF49	1	5	7.90
	2	5	3.10
	Total	10	

Test Statistics[a,b]

	SULF7	SULF21	SULF35	SULF49
Chi-Square	3.153	.278	7.212	6.521
df	1	1	1	1
Asymp. Sig.	.076	.598	.007	.011

a. Kruskal Wallis Test

b. Grouping Variable: Treatment

2. Aerated, difference between continuously wet and dried/rewet floc

2.1 pH, log-transformed, one-way ANOVAs

Test of Homogeneity of Variances

	Levene Statistic	df1	df2	Sig.
TRANSPH7	1.564	1	8	.246
TRANPH21	.353	1	8	.569
TRANPH35	4.066	1	8	.078
TRANPH49	.481	1	8	.508
TRANSPH1	12.368	1	8	.008
TRANPH14	6.087	1	8	.039
TRANPH28	7.007	1	8	.029

ANOVA

		Sum of Squares	df	Mean Square	F	Sig.
TRANSPH7	Between Groups	.000	1	.000	.003	.958
	Within Groups	.003	8	.000		
	Total	.003	9			
TRANPH21	Between Groups	.003	1	.003	10.650	.011
	Within Groups	.002	8	.000		
	Total	.005	9			
TRANPH35	Between Groups	.005	1	.005	46.440	.000
	Within Groups	.001	8	.000		
	Total	.006	9			
TRANPH49	Between Groups	.009	1	.009	66.166	.000
	Within Groups	.001	8	.000		
	Total	.010	9			
TRANSPH1	Between Groups	.009	1	.009	13.269	.007
	Within Groups	.005	8	.001		
	Total	.014	9			
TRANPH14	Between Groups	.003	1	.003	6.355	.036
	Within Groups	.004	8	.000		
	Total	.006	9			
TRANPH28	Between Groups	.003	1	.003	14.883	.005
	Within Groups	.002	8	.000		
	Total	.005	9			

2.1b pH, Kruskall-Wallis

Ranks

	Treatment	N	Mean Rank
PH1	1	5	8.00
	2	5	3.00
	Total	10	
PH7	1	5	5.80
	2	5	5.20
	Total	10	
PH14	1	5	3.40
	2	5	7.60
	Total	10	
PH21	1	5	3.20
	2	5	7.80
	Total	10	
PH28	1	5	3.00
	2	5	8.00
	Total	10	
PH35	1	5	3.00
	2	5	8.00
	Total	10	
PH49	1	5	3.00
	2	5	8.00
	Total	10	

Test Statistics[a,b]

	PH1	PH7	PH14	PH21	PH28	PH35	PH49
Chi-Square	6.818	.098	4.811	5.771	6.860	6.860	6.818
df	1	1	1	1	1	1	1
Asymp. Sig.	.009	.754	.028	.016	.009	.009	.009

a. Kruskal Wallis Test

b. Grouping Variable: Treatment

2.2 EC, Kruskall-Walllis

Ranks

	Treatment	N	Mean Rank
EC1	1	5	3.00
	2	5	8.00
	Total	10	
EC7	1	5	3.00
	2	5	8.00
	Total	10	
EC14	1	5	3.00
	2	5	8.00
	Total	10	
EC21	1	5	3.00
	2	5	8.00
	Total	10	
EC28	1	5	3.40
	2	5	7.60
	Total	10	
EC35	1	5	3.40
	2	5	7.60
	Total	10	
EC49	1	5	3.40
	2	5	7.60
	Total	10	

Test Statistics[a,b]

	EC1	EC7	EC14	EC21	EC28	EC35	EC49
Chi-Square	6.860	6.818	6.818	6.818	4.811	4.811	4.811
df	1	1	1	1	1	1	1
Asymp. Sig.	.009	.009	.009	.009	.028	.028	.028

a. Kruskal Wallis Test

b. Grouping Variable: Treatment

2.3 Iron, log-transformed, one-way ANOVAs

Test of Homogeneity of Variances

	Levene Statistic	df1	df2	Sig.
LGFE7	3.830	1	8	.086
LGFE21	1.764	1	8	.221
LGFE35	49.493	1	8	.000
LGFE49	.350	1	8	.570

ANOVA

		Sum of Squares	df	Mean Square	F	Sig.
LGFE7	Between Groups	.106	1	.106	11.500	.009
	Within Groups	.074	8	.009		
	Total	.180	9			
LGFE21	Between Groups	.007	1	.007	1.275	.292
	Within Groups	.042	8	.005		
	Total	.049	9			
LGFE35	Between Groups	.006	1	.006	2.416	.159
	Within Groups	.021	8	.003		
	Total	.028	9			
LGFE49	Between Groups	.003	1	.003	2.728	.137
	Within Groups	.009	8	.001		
	Total	.012	9			

2.4 Calcium, log-transformed, one-way ANOVAs

Test of Homogeneity of Variances

	Levene Statistic	df1	df2	Sig.
LGCA7	.257	1	8	.626
LGCA21	.064	1	8	.807
LGCA35	1.118	1	8	.321
LGCA49	5.080	1	8	.054

ANOVA

		Sum of Squares	df	Mean Square	F	Sig.
LGCA7	Between Groups	.054	1	.054	2.635	.143
	Within Groups	.165	8	.021		
	Total	.220	9			
LGCA21	Between Groups	.000	1	.000	.003	.958
	Within Groups	.198	8	.025		
	Total	.198	9			
LGCA35	Between Groups	.009	1	.009	.294	.602
	Within Groups	.232	8	.029		
	Total	.241	9			
LGCA49	Between Groups	.049	1	.049	.917	.366
	Within Groups	.426	8	.053		
	Total	.475	9			

2.5 TFP, log-transformed, one-way ANOVAs

Test of Homogeneity of Variances

	Levene Statistic	df1	df2	Sig.
LGP7	.103	1	8	.756
LGP21	.101	1	8	.758
LGP35	10.520	1	8	.012
LGP49	16.220	1	8	.004

ANOVA

		Sum of Squares	df	Mean Square	F	Sig.
LGP7	Between Groups	16.080	1	16.080	323.857	.000
	Within Groups	.397	8	.050		
	Total	16.477	9			
LGP21	Between Groups	12.170	1	12.170	137.692	.000
	Within Groups	.707	8	.088		
	Total	12.877	9			
LGP35	Between Groups	15.740	1	15.740	176.006	.000
	Within Groups	.715	8	.089		
	Total	16.456	9			
LGP49	Between Groups	8.629	1	8.629	97.682	.000
	Within Groups	.707	8	.088		
	Total	9.336	9			

2.6 Sulfate, log-transformed, one-way ANOVAs

Test of Homogeneity of Variances

	Levene Statistic	df1	df2	Sig.
LGS7	1.549	1	8	.249
LGS21	.768	1	8	.406
LGS35	.547	1	8	.481
LGS49	.765	1	8	.407

ANOVA

		Sum of Squares	df	Mean Square	F	Sig.
LGS7	Between Groups	.161	1	.161	4.513	.066
	Within Groups	.285	8	.036		
	Total	.445	9			
LGS21	Between Groups	.241	1	.241	2.050	.190
	Within Groups	.939	8	.117		
	Total	1.179	9			
LGS35	Between Groups	.641	1	.641	7.833	.023
	Within Groups	.655	8	.082		
	Total	1.295	9			
LGS49	Between Groups	.340	1	.340	3.829	.086
	Within Groups	.711	8	.089		
	Total	1.051	9			

3. Continuously wet, difference between anaerobic and aerated floc

3.1 pH, Kruskall-Wallis

Ranks

	Incubation type	N	Mean Rank
PH1	1	5	5.60
	2	5	5.40
	Total	10	
PH7	1	5	5.60
	2	5	5.40
	Total	10	
PH14	1	5	6.00
	2	5	5.00
	Total	10	
PH21	1	5	6.20
	2	5	4.80
	Total	10	
PH28	1	5	5.40
	2	5	5.60
	Total	10	
PH35	1	5	5.70
	2	5	5.30
	Total	10	
PH49	1	5	5.50
	2	5	5.50
	Total	10	

Test Statistics[a,b]

	PH1	PH7	PH14	PH21	PH28	PH35	PH49
Chi-Square	.011	.011	.273	.535	.011	.044	.000
df	1	1	1	1	1	1	1
Asymp. Sig.	.917	.917	.602	.465	.917	.834	1.000

a. Kruskal Wallis Test

b. Grouping Variable: Incubation type

3.2 EC, Kruskall-Wallis

Ranks

	Incubation type	N	Mean Rank
EC1	1	5	6.40
	2	5	4.60
	Total	10	
EC7	1	5	5.80
	2	5	5.20
	Total	10	
EC14	1	5	4.80
	2	5	6.20
	Total	10	
EC21	1	5	4.60
	2	5	6.40
	Total	10	
EC28	1	5	5.20
	2	5	5.80
	Total	10	
EC35	1	5	5.20
	2	5	5.80
	Total	10	
EC49	1	5	4.60
	2	5	6.40
	Total	10	

Test Statistics[a,b]

	EC1	EC7	EC14	EC21	EC28	EC35	EC49
Chi-Square	.884	.098	.535	.884	.098	.098	.884
df	1	1	1	1	1	1	1
Asymp. Sig.	.347	.754	.465	.347	.754	.754	.347

a. Kruskal Wallis Test

b. Grouping Variable: Incubation type

3.3 Iron, log-transformed, one-way ANOVAs

Test of Homogeneity of Variances

	Levene Statistic	df1	df2	Sig.
LGFE7	1.825	1	8	.214
LGFE21	5.243	1	8	.051
LGFE35	7.111	1	8	.029
LGFE49	.891	1	8	.373

ANOVA

		Sum of Squares	df	Mean Square	F	Sig.
LGFE7	Between Groups	.069	1	.069	36.622	.000
	Within Groups	.015	8	.002		
	Total	.084	9			
LGFE21	Between Groups	.020	1	.020	24.286	.001
	Within Groups	.007	8	.001		
	Total	.027	9			
LGFE35	Between Groups	.000	1	.000	1.000	.347
	Within Groups	.000	8	.000		
	Total	.000	9			
LGFE49	Between Groups	.009	1	.009	8.506	.019
	Within Groups	.008	8	.001		
	Total	.017	9			

3.4 Calcium, log-transformed, one-way ANOVAs

Test of Homogeneity of Variances

	Levene Statistic	df1	df2	Sig.
LGCA7	.666	1	8	.438
LGCA21	.973	1	8	.353
LGCA35	14.240	1	8	.005
LGCA49	22.625	1	8	.001

ANOVA

		Sum of Squares	df	Mean Square	F	Sig.
LGCA7	Between Groups	.015	1	.015	1.145	.316
	Within Groups	.106	8	.013		
	Total	.121	9			
LGCA21	Between Groups	.010	1	.010	.722	.420
	Within Groups	.109	8	.014		
	Total	.119	9			
LGCA35	Between Groups	.034	1	.034	1.728	.225
	Within Groups	.159	8	.020		
	Total	.194	9			
LGCA49	Between Groups	.041	1	.041	.999	.347
	Within Groups	.328	8	.041		
	Total	.369	9			

3.5 TFP, log-transformed, one-way ANOVAs

Test of Homogeneity of Variances

	Levene Statistic	df1	df2	Sig.
LGP7	2.031	1	8	.192
LGP21	.300	1	8	.599
LGP35	2.178	1	8	.178
LGP49	1.142	1	8	.316

ANOVA

		Sum of Squares	df	Mean Square	F	Sig.
LGP7	Between Groups	.138	1	.138	3.571	.095
	Within Groups	.309	8	.039		
	Total	.447	9			
LGP21	Between Groups	.021	1	.021	.266	.620
	Within Groups	.624	8	.078		
	Total	.644	9			
LGP35	Between Groups	.053	1	.053	2.822	.131
	Within Groups	.149	8	.019		
	Total	.202	9			
LGP49	Between Groups	.087	1	.087	5.588	.046
	Within Groups	.125	8	.016		
	Total	.211	9			

3.6 Sulfate, log-transformed, one-way ANOVAs

Test of Homogeneity of Variances

	Levene Statistic	df1	df2	Sig.
LGS7	.168	1	8	.693
LGS21	.835	1	8	.388
LGS35	6.782	1	8	.031
LGS49	1.181	1	8	.309

ANOVA

		Sum of Squares	df	Mean Square	F	Sig.
LGS7	Between Groups	.845	1	.845	17.026	.003
	Within Groups	.397	8	.050		
	Total	1.243	9			
LGS21	Between Groups	4.250	1	4.250	79.962	.000
	Within Groups	.425	8	.053		
	Total	4.676	9			
LGS35	Between Groups	3.182	1	3.182	57.976	.000
	Within Groups	.439	8	.055		
	Total	3.621	9			
LGS49	Between Groups	3.544	1	3.544	41.975	.000
	Within Groups	.675	8	.084		
	Total	4.219	9			

4. Dried/rewet, difference between anaerobic and aerated floc

4.1 pH, Kruskall-Wallis

Ranks

	Incubation type	N	Mean Rank
PH1	1	5	3.80
	2	5	7.20
	Total	10	
PH7	1	5	3.00
	2	5	8.00
	Total	10	
PH14	1	5	3.00
	2	5	8.00
	Total	10	
PH21	1	5	3.00
	2	5	8.00
	Total	10	
PH28	1	5	3.00
	2	5	8.00
	Total	10	
PH35	1	5	3.00
	2	5	8.00
	Total	10	
PH49	1	5	3.00
	2	5	8.00
	Total	10	

Test Statistics[a,b]

	PH1	PH7	PH14	PH21	PH28	PH35	PH49
Chi-Square	3.153	6.860	6.818	6.818	6.860	6.860	6.818
df	1	1	1	1	1	1	1
Asymp. Sig.	.076	.009	.009	.009	.009	.009	.009

a. Kruskal Wallis Test

b. Grouping Variable: Incubation type

4.2, EC, one-way ANOVAs

Test of Homogeneity of Variances

	Levene Statistic	df1	df2	Sig.
PH1	1.905	1	8	.205
PH7	.311	1	8	.592
PH14	.315	1	8	.590
PH21	1.765	1	8	.221
PH28	19.059	1	8	.002
PH35	44.476	1	8	.000
PH49	.779	1	8	.403

ANOVA

		Sum of Squares	df	Mean Square	F	Sig.
PH1	Between Groups	.581	1	.581	3.449	.100
	Within Groups	1.347	8	.168		
	Total	1.928	9			
PH7	Between Groups	3.576	1	3.576	28.491	.001
	Within Groups	1.004	8	.126		
	Total	4.580	9			
PH14	Between Groups	7.073	1	7.073	37.684	.000
	Within Groups	1.501	8	.188		
	Total	8.574	9			
PH21	Between Groups	6.790	1	6.790	42.343	.000
	Within Groups	1.283	8	.160		
	Total	8.073	9			
PH28	Between Groups	8.556	1	8.556	62.612	.000
	Within Groups	1.093	8	.137		
	Total	9.649	9			
PH35	Between Groups	8.208	1	8.208	40.588	.000
	Within Groups	1.618	8	.202		
	Total	9.826	9			
PH49	Between Groups	4.122	1	4.122	47.053	.000
	Within Groups	.701	8	.088		
	Total	4.822	9			

4.3 Iron, log-transformed, one-way ANOVAs

Ranks

	Incubation type	N	Mean Rank
FE7	1	5	7.80
	2	5	3.20
	Total	10	
FE21	1	5	7.20
	2	5	3.80
	Total	10	
FE35	1	5	7.10
	2	5	3.90
	Total	10	
FE49	1	5	7.00
	2	5	4.00
	Total	10	

Test Statistics[a,b]

	FE7	FE21	FE35	FE49
Chi-Square	5.771	3.153	2.973	2.455
df	1	1	1	1
Asymp. Sig.	.016	.076	.085	.117

a. Kruskal Wallis Test

b. Grouping Variable: Incubation type

4.4 Calcium, log-transformed, one-way ANOVAs

Test of Homogeneity of Variances

	Levene Statistic	df1	df2	Sig.
LGCA7	.349	1	8	.571
LGCA21	.004	1	8	.951
LGCA35	.007	1	8	.935
LGCA49	1.436	1	8	.265

ANOVA

		Sum of Squares	df	Mean Square	F	Sig.
LGCA7	Between Groups	.100	1	.100	5.481	.047
	Within Groups	.145	8	.018		
	Total	.245	9			
LGCA21	Between Groups	.274	1	.274	11.668	.009
	Within Groups	.188	8	.023		
	Total	.461	9			
LGCA35	Between Groups	.347	1	.347	16.830	.003
	Within Groups	.165	8	.021		
	Total	.511	9			
LGCA49	Between Groups	.287	1	.287	6.583	.033
	Within Groups	.349	8	.044		
	Total	.637	9			

4.5 TFP, log-transformed, one-way ANOVAs

Test of Homogeneity of Variances

	Levene Statistic	df1	df2	Sig.
LGP7	3.007	1	8	.121
LGP21	1.343	1	8	.280
LGP35	4.658	1	8	.063
LGP49	27.329	1	8	.001

ANOVA

		Sum of Squares	df	Mean Square	F	Sig.
LGP7	Between Groups	.177	1	.177	6.072	.039
	Within Groups	.233	8	.029		
	Total	.409	9			
LGP21	Between Groups	.302	1	.302	5.808	.043
	Within Groups	.416	8	.052		
	Total	.719	9			
LGP35	Between Groups	.253	1	.253	2.520	.151
	Within Groups	.803	8	.100		
	Total	1.056	9			
LGP49	Between Groups	.338	1	.338	4.054	.079
	Within Groups	.668	8	.083		
	Total	1.006	9			

4.6 Sulfate, log-transformed, on-way ANOVAs

Test of Homogeneity of Variances

	Levene Statistic	df1	df2	Sig.
LGS7	.013	1	8	.911
LGS21	3.024	1	8	.120
LGS35	.290	1	8	.605
LGS49	3.693	1	8	.091

ANOVA

		Sum of Squares	df	Mean Square	F	Sig.
LGS7	Between Groups	.027	1	.027	2.440	.157
	Within Groups	.088	8	.011		
	Total	.115	9			
LGS21	Between Groups	2.453	1	2.453	9.383	.016
	Within Groups	2.091	8	.261		
	Total	4.544	9			
LGS35	Between Groups	5.256	1	5.256	120.962	.000
	Within Groups	.348	8	.043		
	Total	5.603	9			
LGS49	Between Groups	5.770	1	5.770	76.207	.000
	Within Groups	.606	8	.076		
	Total	6.375	9			

Chapter 5

5.1 P fractionation data (Tables 1-8)

5.2 Primer PCA results (scores and correlation matrices)

5.3 Pearson's correlation matrices and selected scatter graphs

5.4 Incubation charts for Sites 3 and 6

5.5 Efficiency of multiple $MgCl_2$, $NaHCO_3$, CDB and NaOH extractions

Appendix 5.1:

Mass balances of P fractionation data

Table 1: Lake Goollelal sediment phosphorus fractionation data (mg g^{-1} (standard error)) and respective percentages of total extractable phosphorus for two sites (3 and 6). The last column shows the percentages of total P extracted by the scheme of the total sediment P as determined by X-Ray Fluorescence (XRF) analysis.

Site 3 (mg P g^{-1} sediment)	$MgCl_2$-FRP	$NaHCO_3$-FRP	$NaHCO_3$-FNRP	CDB-TFP	NaOH-FRP	NaOH-FNRP	HCl-FRP	HCl-FNRP	Ashed-TFP	Total extractable	Total P
Peat dry	0.022 (0.000)	0.050 (0.002)	0.019 ((0.002)	0.007 (0.001)	0.022 (0.003)	0.216 (0.006)	0.001 (0.000)	0.004 (0.000)	0.077 (0.001)	0.419 (0.015)	0.47
Peat wet	0.033 (0.002)	0.056 (0.014)	0.066 (0.001)	0.030 (0.005)	0.032 (0.004)	0.094 (0.003)	0.001 (0.000)	0.003 (0.000)	0.049 (0.002)	0.365 (0.031)	
Floc dry	1.656 (0.008)	0.178 (0.005)	0.052 (0.001)	0.015 (0.001)	0.022 (0.006)	0.508 (0.014)	0.006 (0.000)	0.008 (0.001)	0.144 (0.002)	2.589 (0.038)	3.31
Floc wet	0.798 (0.044)	0.250 (0.023)	0.149 (0.016)	0.042 (0.006)	0.032 (0.005)	0.537 (0.004)	0.004 (0.001)	0.006 (0.002)	0.078 (0.006)	1.895 (0.107)	

Mean percentage of total extractable										Percentage of total sediment P extracted
Peat dry	5.36	12.05	4.41	1.78	5.32	51.53	0.23	0.98	18.34	89.15
Peat wet	9.04	15.46	18.05	8.32	8.84	25.75	0.35	0.75	13.45	77.66
Floc dry	63.97	6.86	2.02	0.58	0.85	19.62	0.22	0.32	5.55	78.22
Floc wet	42.11	13.18	7.87	2.23	1.68	28.33	0.19	0.32	4.09	57.25

Site 6 (mg P g^{-1} sediment)	$MgCl_2$-FRP	$NaHCO_3$-FRP	$NaHCO_3$-FNRP	CDB-TFP	NaOH-FRP	NaOH-FNRP	HCl-FRP	HCl-FNRP	Ashed-TFP	Total extractable	Total P
Peat dry	0.012 (0.002)	0.056 (0.001)	0.0132 (0.003)	0.019 (0.001)	0.018 (0.001)	0.181 (0.005)	0.0001 (0.000)	0.004 (0.000)	0.052 (0.002)	0.356 (0.015)	0.45
Peat wet	0.047(0.011)	0.035 (0.004)	0.068 (0.005)	0.022 (0.006)	0.036 (0.003)	0.025 (0.005)	0.001 (0.000)	0.005 (0.000)	0.091 (0.003)	0.332 (0.037)	
Floc dry	1.618 (0.011)	0.287 (0.005)	0.052 (0.002)	0.019 (0.003)	0.037 (0.009)	0.578 (0.006)	0.004 (0.000)	0.006 (0.000)	0.119 (0.001)	2.72 (0.037)	3.35
Floc wet	0.650 (0.058)	0.283 ((0.017)	0.241 (0.041)	0.046 (0.011)	0.014 (0.002)	0.459 (0.007)	0.002 (0.000)	0.006 (0.001)	0.080 (001)	1.781 ().138)	

Mean percentage of total extractable										Percentage of total sediment P extracted
Peat dry	3.38	15.81	3.70	5.29	5.05	50.80	0.23	1.03	14.70	79.11
Peat wet	14.17	10.65	20.57	6.74	10.99	7.54	0.38	1.52	27.45	73.78
Floc dry	59.48	10.57	1.90	0.71	1.38	21.25	0.14	0.21	4.37	81.19
Floc wet	36.50	15.86	13.52	2.58	0.78	25.77	0.14	0.33	4.52	53.16

Table 1b: Lake Goollelal sediment filterable phosphorus (mg g^{-1} (standard error)) co-extracted with iron by sodium acetate for two sites (3 and 6).

Site 3 (mg P g^{-1} sediment)	NaOAc
Peat dry	0.08 (0.013)
Peat wet	0.06 (0.024)
Floc dry	1.79 (0.041)
Floc wet	1.53 (0.035)

Site 6 (mg P g^{-1} sediment)	NaOAc
Peat dry	0.08 (0.012)
Peat wet	0.06 (0.017)
Floc dry	1.71 (0.038)
Floc wet	1.41 (0.132)

Table 2: Lake Goollelal sediment iron co-extracted with phosphorus fractions (mg g^{-1} (standard error)) and respective percentages of total extractable iron for two sites (3 and 6). The last column shows the percentages of total iron extracted by the scheme of the total sediment iron as determined by X-Ray Fluorescence (XRF) analysis.

Site 3 (mg Fe g^{-1} sediment)	$MgCl_2$	$NaHCO_3$	CDB	NaOH	HCl	Ashed	Total extractable	Total Fe
Peat dry	0.02 (0.001)	1.68 (0.037)	2.12 (0.017)	0.66 (0.034)	2.81 (0.128)	0.11 (0.009)	7.40 (0.226)	27.80
Peat wet	0.68 (0.032)	4.08 (0.672)	1.82 (0.045)	2.49 (0.347)	3.48 (0.200)	0.53 (0.015)	13.09 (1.311)	
Floc dry	0.03 (0.001)	1.78 (0.027)	0.90 (0.011)	0.78 (0.037)	2.41 (0.053)	0.14 (0.0.007)	6.05 (0.136)	29.70
Floc wet	0.24 (0.025)	1.62 (0.058)	0.37 (0.043)	0.72 (0.060)	1.51 (0.213)	0.43 (0.084)	4.88 (0.483)	
Mean percentage of total extractable								**Percentage of total sediment Fe extracted**
Peat dry	0.20	22.75	28.59	8.92	38.00	1.55		26.61
Peat wet	5.18	31.19	13.92	19.03	26.62	4.06		47.07
Floc dry	0.47	29.41	14.91	12.97	39.91	2.33		20.36
Floc wet	4.90	33.07	7.55	14.79	30.81	8.87		16.44

Site 6 (mg Fe g^{-1} sediment)	$MgCl_2$	$NaHCO_3$	CDB	NaOH	HCl	Ashed	Total extractable	Total Fe
Peat dry	0.68 (0.007)	6.13 (0.048)	3.73 (0.051)	0.59 (0.001)	3.83 (0.168)	0.09 (0.005)	15.05 (0.280)	58.60
Peat wet	1.15 (0.277)	2.29 (0.189)	3.50 (0.434)	1.76 (0.267)	9.17 (0.871)	0.39 (0.056)	18.26 (2.094)	
Floc dry	0.15 (0.006)	3.74 (0.042)	0.94 (0.019)	1.49 (0.020)	5.22 (0.050)	0.19 (0.013)	11.73 (0.150)	64.90
Floc wet	0.64 (0.058)	1.97 (0.178)	0.86 (0.126)	1.76 (0.134)	5.02 (0.166)	0.62 (0.159)	10.87 (0.821)	
Mean percentage of total extractable								**Percentage of total sediment Fe extracted**
Peat dry	4.50	40.71	24.79	3.94	25.44	0.62		25.68
Peat wet	6.31	12.52	19.19	9.62	50.22	2.13		31.16
Floc dry	1.31	31.85	8.03	12.66	44.52	1.63		18.08
Floc wet	5.85	18.15	7.88	16.21	46.18	5.73		16.75

Table 3: Lake Goollelal sediment manganese co-extracted with phosphorus fractions (mg g^{-1} (standard error)) and respective percentages of total extractable manganese for two sites (3 and 6). The last column shows the percentages of total manganese extracted by the scheme of the total sediment manganese as determined by X-Ray Fluorescence (XRF) analysis.

Site 3 (mg Mn g^{-1} sediment)	$MgCl_2$	$NaHCO_3$	CDB	NaOH	HCl	Ashed	Total extractable	Total Mn
Peat dry	0.0259 (0.000)	0.0122 (0.003)	0.0014 (0.000)	0.0009 (0.0000)	0.0038 ((0.000)	0.0026 (0.001)	0.047 (0.004)	0.033
Peat wet	0.0239 (0.003)	0.0217 (0.005)	0.0062 (0.000)	0.0044 ((0.001)	0.0076 (0.001)	0.0022 ((0.000)	0.066 (0.010)	
Floc dry	0.0342 (0.001)	0.0100 (0.001)	0.0017 (0.000)	0.0010 (0.000)	0.0051 (0.000)	0.0184 (0.000)	0.070 (0.002)	0.089
Floc wet	0.0772 (0.009)	0.0298 (0.003)	0.0036 (0.000)	0.0026 (0.000)	0.0080 (0.001)	0.0062 ((0.000)	0.127 (0.012)	

Mean percentage of total extractable							Percentage of total sediment Mn extracted
Peat dry	36.26	32.81	9.45	6.71	11.49	3.29	142
Peat wet	36.26	32.81	9.45	6.71	11.49	3.29	200
Floc dry	48.53	14.23	2.40	1.42	7.31	26.10	79
Floc wet	60.64	23.42	2.81	2.03	6.26	4.84	143

Site 6 (mg Mn g^{-1} sediment)	$MgCl_2$	$NaHCO_3$	CDB	NaOH	HCl	Ashed	Total extractable	Total Mn
Peat dry	0.0155 (0.000)	0.0114 (0.000)	0.0013 (0.000)	0.0009 (0.000)	0.0024 (0.000)	0.0021 (0.000)	0.034 (0.000)	0.021
Peat wet	0.0167 (0.004)	0.0148 (0.004)	0.0029 (0.000)	0.0027 (0.000)	0.0039 (0.000)	0.0016 (0.000)	0.043 (0.008)	
Floc dry	0.0278 (0.004)	0.0097 (0.001)	0.0018 (0.000)	0.0013 (0.000)	0.0039 (0.000)	0.0153 (0.001)	0.060 (0.006)	0.050
Floc wet	0.0602 (0.003)	0.0243 (0.002)	0.0035 (0.001)	0.0034 (0.000)	0.0065 (0.000)	0.0048 (0.000)	0.103 (0.006)	

Mean percentage of total extractable							Percentage of total sediment Mn extracted
Peat dry	45.92	33.93	3.94	2.63	7.27	6.31	160
Peat wet	39.26	34.83	6.70	6.23	9.18	3.80	203
Floc dry	46.56	16.16	2.94	2.14	6.59	25.62	119
Floc wet	58.55	23.67	3.44	3.30	6.35	4.69	205

Table 4: Lake Goollelal sediment aluminium co-extracted with phosphorus fractions (mg g^{-1} (standard error)) and respective percentages of total extractable aluminium for two sites (3 and 6). The last column shows the percentages of total aluminium extracted by the scheme of the total sediment aluminium as determined by X-Ray Fluorescence (XRF) analysis.

Site 3 (mg Al g^{-1} sediment)	$MgCl_2$	$NaHCO_3$	CDB	NaOH	HCl	Ashed	Total extractable	Total Al
Peat dry	0.004 (0.000)	0.098 (0.009)	0.266 (0.003)	0.538*	0.042 (0.002)	1.218 (0.022)	2.17 (0.036)	3.20
Peat wet	0.060 (0.022)	0.242 (0.054)	0.156 (0.004)	0.449*	0.052 (0.002)	1.008 (0.041)	1.97 (0.123)	
Floc dry	0.007 (0.002)	0.079 (0.005)	0.159 (0.002)	0.778*	0.090 (0.002)	2.807 (0.020)	3.92 (0.031)	5.90
Floc wet	0.024 (0.010)	0.095 (0.005)	0.072 (0.009)	0.435*	0.065 (0.002)	1.602 (0.152)	2.29 (0.178)	

Mean percentage of total extractable							Percentage of total sediment Al extracted
Peat dry	0.18	4.54	12.27	24.84	1.95	56.23	67.81
Peat wet	3.03	12.33	7.90	22.84	2.64	51.26	61.56
Floc dry	0.17	2.02	4.06	19.84	2.30	71.59	66.45
Floc wet	1.03	4.13	3.15	18.98	2.84	69.87	38.81

Site 6 (mg Al g^{-1} sediment)	$MgCl_2$	$NaHCO_3$	CDB	NaOH	HCl	Ashed	Total extractable	Total Al
Peat dry	0.032 (0.001)	0.274 (0.004)	0.421 (0.007)	0.609*	0.048 (0.002)	1.360 (0.036)	2.74 (0.050)	4.10
Peat wet	0.018 (0.006)	0.282 (0.032)	0.228 (0.009)	0.382*	0.045 (0.002)	1.105 (0.142)	2.06 (0.191)	
Floc dry	0.007 (0.004)	0.072 (0.003)	0.125 (0.003)	0.594*	0.064 (0.002)	1.718 (0.033)	2.58 (0.045)	4.60
Floc wet	0.010 (0.003)	0.067 (0.004)	0.088 (0.004)	0.272*	0.057 (0.008)	1.289 (0.037)	1.78 (0.056)	

Mean percentage of total extractable							Percentage of total sediment Al extracted
Peat dry	1.16	9.99	15.35	22.20	1.73	49.57	66.83
Peat wet	0.87	13.67	11.07	18.55	2.20	53.65	50.24
Floc dry	0.27	2.80	4.86	23.02	2.48	66.57	56.10
Floc wet	0.57	3.77	4.92	15.25	3.20	72.29	38.69

Table 5: Lake Goollelal sediment calcium co-extracted with phosphorus fractions (mg g^{-1} (standard error)) and respective percentages of total extractable calcium for two sites (3 and 6). The last column shows the percentages of total calcium extracted by the scheme of the total sediment calcium as determined by X-Ray Fluorescence (XRF) analysis.

Site 3 (mg Ca g^{-1} sediment)	$MgCl_2$	$NaHCO_3$	CDB	NaOH	HCl	Ashed	Total extractable	Total Ca
Peat dry	17.62 (0.431)	1.75 (0.034)	0.27 (0.021)	0.03*	0.05 (0.002)	0.04 (0.007)	19.76 (0.494)	20
Peat wet	12.13 (0.713)	4.02 (0.877)	0.22 (0.043)	0.04*	0.07 (0.002)	0.07 (0.004)	16.54 (1.639)	
Floc dry	17.05 (0.110)	1.18 (0.006)	0.20 (0.003)	0.03*	0.10 (0.001)	0.04 (0.007)	18.61 (0.127)	17
Floc wet	14.28 (0.601)	2.83 (0.110)	0.18 (0.019)	0.06*	0.09 (0.003)	0.07 (0.009)	17.51 (0.742)	
Mean percentage of total extractable								**Percentage of total sediment Ca extracted**
Peat dry	89.17	8.84	1.36	0.16	0.26	0.21		98.81
Peat wet	73.30	24.29	1.30	0.27	0.44	0.39		82.70
Floc dry	91.61	6.33	1.08	0.18	0.56	0.24		109.45
Floc wet	81.56	16.15	1.03	0.31	0.52	0.42		103.00

Site 6 (mg Ca g^{-1} sediment)	$MgCl_2$	$NaHCO_3$	CDB	NaOH	HCl	Ashed	Total extractable	Total Ca
Peat dry	7.60 (0.034)	2.05 (0.061)	0.25 (0.016)	0.03*	0.05 (0.001)	0.04 (0.005)	10.02 (0.117)	8
Peat wet	5.09 (1.10)	1.95 (0.092)	0.12 (0.019)	0.03*	0.08 (0.011)	0.05 (0.007)	7.33 (1.23)	
Floc dry	10.44 (0.088)	1.18 (0.011)	0.16 (0.003)	0.03*	0.10 (0.006)	0.04 (0.006)	11.94 (0.114)	12
Floc wet	10.17 (0.332)	2.13 (0.059)	0.12 (0.003)	0.03*	0.10 (0.013)	0.06 (0.02)	12.60 (0.427)	
Mean percentage of total extractable								**Percentage of total sediment Ca extracted**
Peat dry	75.85	20.46	2.50	0.30	0.50	0.39		125.23
Peat wet	69.49	26.66	1.61	0.35	1.14	0.75		91.59
Floc dry	87.44	9.88	1.30	0.26	0.82	0.29		99.47
Floc wet	80.71	16.87	0.93	0.25	0.79	0.45		104.99

Table 6: Lake Goollelal sediment sulfur co-extracted with phosphorus $MgCl_2$ and $NaHCO_3$ fractions (mg g^{-1} (standard error)) and respective percentages of total extractable sulfur for two sites (3 and 6). The last column shows the percentages of sulfur extracted by the two reagents of the total sediment sulfur as determined by analysis with a Leico Total Sulfur Analyser.

Site 3 (mg S g^{-1} sediment)	$MgCl_2$	$NaHCO_3$	Total extracted	Total S
Peat dry	3.69 (0.092)	3.98 (0.057)	7.67 (0.149)	51.20
Peat wet	9.31 (0.879)	2.76 (0.407)	12.07 (1.29)	
Floc dry	5.63 (0.230)	2.81 (0.076)	8.44 (0.306)	52.60
Floc wet	21.39 (1.79)	1.16 (0.210)	22.55 (2.00)	

Mean percentage of total extractable			Percentage of total sediment S extracted
Peat dry	48.14	51.86	14.98
Peat wet	77.14	22.86	23.58
Floc dry	66.74	33.26	16.05
Floc wet	94.85	5.15	42.88

Site 6 (mg S g^{-1} sediment)	$MgCl_2$	$NaHCO_3$	Total extracted	Total S
Peat dry	1.74 (0.022)	5.39 (0.086)	7.13 (0.108)	61.30
Peat wet	1.55 (0.445)	1.32 (0.112)	2.87 (0.557)	
Floc dry	1.97 (0.123)	4.25 (0.101)	6.23 (0.224)	75.70
Floc wet	6.79 (0.330)	1.33 (0.211)	8.12 (0.541)	

Mean percentage of total extractable			Percentage of total sediment S extracted
Peat dry	24.37	75.63	11.63
Peat wet	54.08	45.92	4.69
Floc dry	31.69	68.31	8.23
Floc wet	83.67	16.33	10.72

Table 7a: Gilvin (g440) extracted by the three reagents $NaHCO_3$, CDB and NaOH from Goollelal sediments from two sites (3 and 6). Gilvin is expressed as gilvin g^{-1} sediment L^{-1}. (SE in brackets, n=3)

Site 3	$NaHCO_3$	CDB	NaOH	Total
Peat dry	22(0)	15 (0)	237 (1)	274
Peat wet	18 (3)	16 (1)	183 (8)	218
Floc dry	9 (1)	6 (0)	90 (1)	104
Floc wet	6 (0)	5 (0)	56 (6)	66
Site 6				
Peat dry	21 (0)	11 (0)	171 (1)	203
Peat wet	8 (1)	11 (3)	128 (7)	147
Floc dry	7 (0)	3 (0)	44 (1)	54
Floc wet	4 (0)	3 (0)	36 (1)	44

Table 7b: Gilvin (g440) extracted by the three reagents $NaHCO_3$, CDB and NaOH from Goollelal (means of sites 3 and 6). Gilvin is expressed as gilvin g^{-1} sediment L^{-1}.)

	$NaHCO_3$	CDB	NaOH	Total
Peat dry	22	13	204	238
Peat wet	13	14	156	182
Floc dry	8	5	67	79
Floc wet	5	4	46	55

Table 7c: Proportion of total gilvin (g440) extracted by the three reagents $NaHCO_3$, CDB and NaOH from Goollelal (mean of sites 3 and 6). Figures are percentages.

	$NaHCO_3$	CDB	NaOH	Total
Peat dry	9.1	5.5	85.5	100
Peat wet	7.2	7.6	85.2	100
Floc dry	10.1	5.7	84.2	100
Floc wet	9.4	7.3	83.3	100

Table 8: Lake Goollelal sediment phosphorus fractionation data (mg g^{-1} (standard error)) and respective percentages of total extractable phosphorus for two sites (3 and 6). The extraction scheme of Hall (1996) was used. Note the differences in P retention between wet and dried sediments after addition of pyro-phosphate. The last column shows the percentages of total P extracted by the scheme of the total sediment P as determined by X-Ray Fluorescence (XRF) analysis. (Total P was determined by ICP-AES).

Site 3 (mg P g^{-1} sediment)	NaOAc	Pyro-P	0.25 M NH_2.OH.HCl	1 M NH_2.OH.HCl	$KClO_3$	Residual	Total extractable	Total P
Peat dry	0.08 (0.013)	79.41	2.91	0.19	0.09	0.06	82.73	0.47
Peat wet	0.06 (0.024)	232.42	17.90	1.07	0.07	0.05	251.58	
Floc dry	1.79 (0.041)	131.15	3.65	0.33	0.14	0.10	137.16	3.31
Floc wet	1.53 (0.035)	307.52	17.98	1.14	0.11	0.10	328.37	
Site 6 (mg P g^{-1} sediment)								**Percentage of total sediment P extracted**
Peat dry	0.10	95.98	3.51	0.23	0.11	0.07	100	17602.90
Peat wet	0.03	92.38	7.11	0.43	0.03	0.02	100	53528.60
Floc dry	1.30	95.62	2.66	0.24	0.10	0.07	100	4143.75
Floc wet	0.47	93.65	5.48	0.35	0.03	0.03	100	9920.67

Site 6 (mg P/g sediment)	NaOAc	Pyro-P	0.25 M NH_2.OH.HCl	1 M NH_2.OH.HCl	$KClO_3$	Residual	Total extractable	Total P
Peat dry	0.08 (0.012)	55.62	1.73	0.15	0.06	0.06	57.70	0.45
Peat wet	0.06 (0.017)	259.57	17.90	0.91	0.06	0.06	278.57	
Floc dry	1.71 (0.038)	113.82	3.24	0.31	0.09	0.07	119.24	3.35
Floc wet	1.41 (0.132)	237.48	12.74	0.82	0.08	0.06	252.59	
Mean percentage of total extractable								**Percentage of total sediment P extracted**
Peat dry	0.14	96.40	2.99	0.25	0.11	0.10	100	12822.06
Peat wet	0.02	93.18	6.43	0.33	0.02	0.02	100	61904.15
Floc dry	1.44	95.45	2.72	0.26	0.07	0.06	100	3559.50
Floc wet	0.56	94.02	5.04	0.32	0.03	0.02	100	7539.95

Appendix 5.2:

P fractionation Primer PCA scores and correlations

PCA
Principal Component Analysis

Worksheet

$MgCl_2$ extracts
Sample selection: All
Variable selection: 1-6 (MgCl2)

Eigenvalues

PC	Eigenvalues	%Variation	Cum.%Variation
1	2.70	45.1	45.1
2	1.59	26.5	71.6
3	0.85	14.2	85.8
4	0.57	9.5	95.2

Eigenvectors
(Coefficients in the linear combinations of variables making up PC's)

Variable	PC1	PC2	PC3	PC4
FRP-MgCl2	-0.407	-0.286	-0.314	0.754
Fe-MgCl2	0.489	0.272	-0.400	-0.070
Mn-MgCl2	-0.415	0.453	-0.434	-0.120
Al-MgCl2	0.263	0.490	0.522	0.579
Ca-MgCl2	-0.485	-0.052	0.529	-0.277
S-MgCl2	-0.343	0.630	-0.020	-0.014

Principal Component Scores

Sample	SCORE1	SCORE2	SCORE3	SCORE4
3-1 P wet	1.878	1.973	2.198	1.632
3-2 P wet	0.934	1.118	1.100	0.099
3-3 P wet	0.495	0.833	0.340	-0.590
3-1 F wet	-1.870	2.803	0.167	0.510
3-2 F wet	-2.791	2.318	-0.965	-0.433
3-3 F wet	-1.935	1.361	-0.330	-0.320
3-1 P dry	-0.680	-0.870	1.203	-1.277
3-2 P dry	-0.766	-0.960	1.351	-1.361
3-3 P dry	-0.626	-0.962	1.131	-1.298
3-1 F dry	-1.799	-1.199	0.373	0.610
3-2 F dry	-1.843	-1.294	0.167	0.472
3-3 F dry	-1.826	-1.059	0.292	0.604
6-1 P wet	2.503	-0.418	-0.858	-0.250
6-2 P wet	2.837	0.722	-1.089	-0.210
6-3 P wet	2.258	-0.677	-0.802	-0.258
6-1 F wet	-0.286	0.492	-0.803	-0.004
6-2 F wet	-0.218	0.550	-1.501	-0.394
6-3 F wet	-0.159	0.289	-1.095	-0.423
6-1 P dry	1.881	-0.124	0.223	0.023
6-2 P dry	1.840	-0.222	0.197	-0.051
6-3 P dry	1.907	-0.169	0.209	0.003
6-1 F dry	-0.553	-1.517	-0.489	0.951
6-2 F dry	-0.643	-1.199	-0.444	1.098
6-3 F dry	-0.538	-1.789	-0.573	0.866

$MgCl_2$ extracts

Sample selection: All
Variable selection: 1,2,4-6 (without Mn)

Eigenvalues

PC	Eigenvalues	%Variation	Cum.%Variation
1	2.40	48.0	48.0
2	1.29	25.8	73.8
3	0.62	12.4	86.1
4	0.50	10.1	96.2

Eigenvectors
(Coefficients in the linear combinations of variables

making up PC's)

Variable	PC1	PC2	PC3	PC4
FRP-MgCl2	-0.467	0.223	0.756	0.303
Fe-MgCl2	0.584	0.030	0.235	-0.318
Al-MgCl2	0.346	-0.586	0.080	0.727
Ca-MgCl2	-0.532	-0.275	-0.487	0.050
S-MgCl2	-0.196	-0.729	0.360	-0.524

Principal Component Scores

Sample	SCORE1	SCORE2	SCORE3	SCORE4
3-1 P wet	2.021	-2.397	-0.060	2.210
3-2 P wet	0.971	-1.416	-0.306	0.254
3-3 P wet	0.628	-0.830	-0.369	-0.582
3-1 F wet	-0.775	-2.746	0.941	-0.384
3-2 F wet	-1.419	-1.672	0.653	-1.176
3-3 F wet	-1.223	-1.274	0.392	-0.912
3-1 P dry	-1.062	0.115	-1.739	-0.133
3-2 P dry	-1.204	0.089	-1.872	-0.142
3-3 P dry	-1.037	0.228	-1.722	-0.175
3-1 F dry	-2.172	0.372	0.243	0.535
3-2 F dry	-2.186	0.583	0.214	0.410
3-3 F dry	-2.109	0.331	0.263	0.534
6-1 P wet	2.169	1.056	0.247	-0.568
6-2 P wet	2.987	0.421	0.415	-0.593
6-3 P wet	1.883	1.251	0.116	-0.416
6-1 F wet	0.146	0.099	0.380	-0.228
6-2 F wet	0.403	0.507	0.423	-0.709
6-3 F wet	0.273	0.491	0.167	-0.550
6-1 P dry	1.608	0.294	-0.268	0.312
6-2 P dry	1.533	0.368	-0.297	0.229
6-3 P dry	1.612	0.332	-0.270	0.281
6-1 F dry	-1.017	1.253	0.823	0.548
6-2 F dry	-0.920	1.070	0.803	0.848
6-3 F dry	-1.113	1.477	0.826	0.407

$NaHCO_3$ extracts

Sample selection: All
Variable selection: 7,8,10-15

Eigenvalues

PC	Eigenvalues	%Variation	Cum.%Variation
1	4.14	51.7	51.7
2	2.15	26.9	78.6
3	0.88	11.0	89.6
4	0.59	7.4	97.0

Eigenvectors
(Coefficients in the linear combinations of variables making up PC's)

Variable	PC1	PC2	PC3	PC4
FNRP-NaHCO3	0.437	-0.153	-0.222	-0.075
FRP-NaHCO3	0.373	0.288	-0.514	-0.004
Fe-NaHCO3	-0.350	-0.116	-0.674	-0.323
Mn-NaHCO3	0.335	-0.456	-0.171	0.225
Al-NaHCO3	-0.309	-0.418	0.108	-0.601
Ca-NaHCO3	0.016	-0.638	-0.176	0.285
S-NaHCO3	-0.402	0.264	-0.398	0.253
gilvin-NaHCO3	-0.421	-0.141	0.032	0.577

Principal Component Scores

Sample	SCORE1	SCORE2	SCORE3	SCORE4
Peat wet 3	-1.021	-2.414	-0.325	0.403
Floc wet 3	2.581	-0.965	-0.198	0.362
Peat dry 3	-1.336	0.724	1.037	1.366
Floc dry 3	0.293	1.643	0.689	-0.066
Peat wet 6	-0.218	-0.738	1.429	-1.328
Floc wet 6	2.985	-0.110	-0.584	-0.063
Peat dry 6	-3.229	-0.247	-1.041	-0.372
Floc dry 6	-0.055	2.107	-1.008	-0.302

CDB extracts

Sample selection: All

Variable selection: 16-21

Eigenvalues

PC	Eigenvalues	%Variation	Cum.%Variation
1	3.39	56.4	56.4
2	1.38	22.9	79.4
3	0.83	13.9	93.2
4	0.36	6.0	99.2

Eigenvectors
(Coefficients in the linear combinations of variables making up PC's)

Variable	PC1	PC2	PC3	PC4
TFP-CDB	0.440	0.284	-0.237	0.705
Fe-CDB	-0.429	0.190	-0.626	-0.003
Mn-CDB	0.250	0.746	0.070	-0.075
Al-CDB	-0.506	-0.024	-0.277	0.414
Ca-CDB	-0.397	0.065	0.670	0.490
gilvin-CDB	-0.381	0.567	0.147	-0.292

Principal Component Scores

Sample	SCORE1	SCORE2	SCORE3	SCORE4
Peat wet 3	0.090	2.494	0.639	-0.213
Floc wet 3	2.038	0.067	0.496	0.606
Peat dry 3	-2.267	-0.219	1.042	-0.230
Floc dry 3	0.056	-1.125	0.700	-0.327
Peat wet 6	-0.526	0.408	-1.655	-0.761
Floc wet 6	2.453	-0.018	-0.622	0.394
Peat dry 6	-2.712	-0.240	-0.679	0.991
Floc dry 6	0.868	-1.368	0.080	-0.459

NaOH extracts

Sample selection: All
Variable selection: 22,23,25,27,29

Eigenvalues

PC	Eigenvalues	%Variation	Cum.%Variation
1	1.91	38.3	38.3
2	1.65	32.9	71.2
3	0.97	19.4	90.6
4	0.36	7.2	97.8

Eigenvectors
(Coefficients in the linear combinations of variables making up PC's)

Variable	PC1	PC2	PC3	PC4
FNRP-NaOH	0.616	-0.364	-0.007	0.071
FRP-NaOH	-0.237	-0.320	-0.831	-0.381
Fe-NaOH	-0.518	-0.423	-0.007	0.725
Al-NaOH	0.407	0.403	-0.551	0.569
gilvin-NaOH	-0.361	0.651	-0.076	-0.029

Principal Component Scores

Sample	SCORE1	SCORE2	SCORE3	SCORE4
Peat wet 3	-2.170	-0.127	-0.393	0.709
Floc wet 3	0.989	-0.937	-0.178	-0.979
Peat dry 3	-0.214	1.857	0.226	-0.414
Floc dry 3	1.855	0.619	-0.477	0.739
Peat wet 6	-1.827	-0.374	-0.467	-0.472
Floc wet 6	0.153	-1.384	2.101	0.273
Peat dry 6	0.351	1.702	0.422	-0.039
Floc dry 6	0.863	-1.355	-1.235	0.182

HCl extracts

Sample selection: All
Variable selection: 30,31,33-36

Eigenvalues

PC	Eigenvalues	%Variation	Cum.%Variation
1	3.72	62.0	62.0

2	1.27	21.1	83.1
3	0.84	14.0	97.1
4	0.10	1.7	98.8

Eigenvectors
(Coefficients in the linear combinations of variables making up PC's)

Variable	PC1	PC2	PC3	PC4
FNRP-HCl	-0.467	-0.277	-0.182	-0.774
FRP-HCl	-0.506	-0.037	-0.151	0.133
Fe-HCl	0.176	-0.740	0.467	0.105
Mn-HCl	-0.217	0.561	0.707	-0.175
Al-HCl	-0.496	0.012	-0.206	0.562
Ca-HCl	-0.449	-0.244	0.429	0.162

Principal Component Scores

Sample	SCORE1	SCORE2	SCORE3	SCORE4
Peat wet 3	1.119	1.405	0.971	0.399
Floc wet 3	-1.507	1.401	0.403	-0.136
Peat dry 3	1.861	0.577	-0.943	-0.444
Floc dry 3	-3.432	-0.284	-0.939	0.030
Peat wet 6	1.251	-1.881	0.853	-0.098
Floc wet 6	-0.645	-0.226	0.952	-0.348
Peat dry 6	2.157	-0.033	-1.163	0.221
Floc dry 6	-0.803	-0.961	-0.134	0.375

Ashed/HCl extracts

Sample selection: All
Variable selection: 37-41

Eigenvalues

PC	Eigenvalues	%Variation	Cum.%Variation
1	3.42	68.5	68.5
2	0.83	16.6	85.0
3	0.50	10.0	95.1
4	0.16	3.2	98.2

Eigenvectors
(Coefficients in the linear combinations of variables making up PC's)

Variable	PC1	PC2	PC3	PC4
TFP-Ashed	0.484	-0.337	-0.167	0.690
Fe-Ashed	-0.414	0.045	-0.905	0.080
Mn-Ashed	0.435	-0.541	-0.284	-0.661
Al-Ashed	-0.501	-0.268	0.221	-0.157
Ca-Ashed	0.392	0.721	-0.151	-0.236

Principal Component Scores

Sample	SCORE1	SCORE2	SCORE3	SCORE4
Peat wet 3	-3.290	-0.229	-1.189	0.096
Floc wet 3	1.774	-0.607	-0.269	0.467
Peat dry 3	-2.380	-0.494	1.315	-0.150
Floc dry 3	0.631	1.713	-0.162	-0.267
Peat wet 6	1.259	-0.706	0.113	0.309
Floc wet 6	1.471	-0.945	-0.290	-0.763
Peat dry 6	0.140	0.607	0.411	0.342
Floc dry 6	0.396	0.661	0.071	-0.034

Ashed/HCl extracts

Sample selection: All
Variable selection: 37-40

Eigenvalues

PC	Eigenvalues	%Variation	Cum.%Variation
1	2.99	74.7	74.7
2	0.52	13.1	87.8
3	0.34	8.6	96.4
4	0.14	3.6	100.0

Eigenvectors

(Coefficients in the linear combinations of variables making up PC's)

Variable	PC1	PC2	PC3	PC4
TFP-Ashed	-0.541	0.253	-0.048	-0.801
Fe-Ashed	0.449	0.832	0.320	-0.059
Mn-Ashed	-0.502	0.493	-0.480	0.523
Al-Ashed	0.504	0.022	-0.815	-0.285

Principal Component Scores

Sample	SCORE1	SCORE2	SCORE3	SCORE4
Peat wet 3	3.004	1.226	0.192	-0.074
Floc wet 3	-1.787	0.435	-0.212	-0.627
Peat dry 3	1.990	-0.975	-0.999	-0.064
Floc dry 3	0.090	-0.335	0.620	0.176
Peat wet 6	-1.448	0.054	-0.134	-0.247
Floc wet 6	-1.615	0.589	-0.558	0.691
Peat dry 6	-0.056	-0.679	0.632	-0.035
Floc dry 6	-0.179	-0.315	0.459	0.180

$NaHCO_3$ and NaOH combined

Sample selection: All
Variable selection: 7-10,12,14,15,22-25,27,29 (NaHCO3 and NaOH)

Eigenvalues

PC	Eigenvalues	%Variation	Cum.%Variation
1	6.75	51.9	51.9
2	2.91	22.4	74.3
3	1.34	10.3	84.6
4	1.13	8.7	93.2
5	0.49	3.8	97.0

Eigenvectors
(Coefficients in the linear combinations of variables making up PC's)

Variable	PC1	PC2	PC3	PC4	PC5
FNRP-NaHCO3	0.301	-0.278	0.277	0.219	0.044
FRP-NaHCO3	0.364	0.116	-0.115	0.185	-0.111
TFP-NaHCO3	0.372	-0.048	0.048	0.218	-0.053
Fe-NaHCO3	-0.213	0.106	-0.280	0.691	0.154
Al-NaHCO3	-0.300	-0.250	-0.167	0.184	0.520
S-NaHCO3	-0.214	0.412	-0.104	0.330	-0.246
gilvin-NaHCO3	-0.338	0.143	0.214	0.100	-0.354
FNRP-NaOH	0.327	0.300	-0.081	0.025	-0.068
FRP-NaOH	-0.012	-0.161	-0.733	-0.353	-0.103
TFP-NaOH	0.327	0.294	-0.110	0.011	-0.072
Fe-NaOH	0.003	-0.442	-0.296	0.225	-0.594
Al-NaOH	-0.092	0.495	-0.209	-0.187	0.114
gilvin-NaOH	-0.348	0.017	0.241	-0.170	-0.343

Principal Component Scores

Sample	SCORE1	SCORE2	SCORE3	SCORE4	SCORE5
Peat wet 3	-2.268	-1.734	-0.659	0.444	-0.856
Floc wet 3	2.798	-0.098	-0.057	-0.670	0.556
Peat dry 3	-2.126	1.027	1.455	-1.150	-0.827
Floc dry 3	1.024	1.913	0.083	-0.928	0.327
Peat wet 6	-1.509	-2.562	-0.636	-0.940	0.746
Floc wet 6	3.556	-1.404	1.501	1.210	-0.203
Peat dry 6	-3.259	1.469	0.320	1.578	0.833
Floc dry 6	1.783	1.391	-2.007	0.455	-0.576

All extracts and all variables combined

Worksheet

Sample selection: All
Variable selection: All

Eigenvalues

PC	Eigenvalues	%Variation	Cum.%Variation
1	16.88	41.2	41.2
2	9.99	24.4	65.5
3	6.12	14.9	80.5

4	2.93	7.1	87.6
5	2.13	5.2	92.8

Eigenvectors
(Coefficients in the linear combinations of variables making up PC's)

Variable	PC1	PC2	PC3	PC4	PC5
FRP-MgCl2	0.188	0.153	0.031	0.227	0.016
Fe-MgCl2	-0.088	-0.188	-0.274	0.062	0.077
Mn-MgCl2	0.196	-0.106	0.096	-0.240	0.072
Al-MgCl2	-0.107	-0.205	0.107	0.192	0.308
Ca-MgCl2	0.060	0.101	0.343	-0.078	-0.187
S-MgCl2	0.124	-0.154	0.205	-0.128	0.197
FNRP-NaHCO3	0.168	-0.179	-0.063	-0.170	-0.057
FRP-NaHCO3	0.221	0.014	-0.002	-0.012	0.049
TFP-NaHCO3	0.219	-0.070	-0.029	-0.084	0.007
Fe-NaHCO3	-0.138	0.018	-0.058	0.130	0.449
Mn-NaHCO3	0.098	-0.259	0.082	-0.181	0.100
Al-NaHCO3	-0.183	-0.100	-0.140	0.114	0.221
Ca-NaHCO3	-0.061	-0.271	0.155	0.041	0.151
S-NaHCO3	-0.135	0.199	0.060	0.025	0.198
gilvin-NaHCO3	-0.217	0.053	0.147	-0.092	0.054
TFP-CDB	0.136	-0.237	-0.035	-0.103	0.162
Fe-CDB	-0.205	0.016	-0.194	-0.037	0.091
Mn-CDB	0.003	-0.286	0.107	0.188	0.001
Al-CDB	-0.198	0.122	-0.083	-0.125	0.200
Ca-CDB	-0.143	0.119	0.264	-0.130	0.134
gilvin-CDB	-0.218	-0.065	0.113	0.021	-0.120
FNRP-NaOH	0.212	0.106	0.080	-0.022	0.082
FRP-NaOH	0.002	-0.067	-0.027	0.329	-0.039
TFP-NaOH	0.213	0.104	0.079	-0.010	0.081
Fe-NaOH	-0.020	-0.221	-0.063	0.329	-0.195
Mn-NaOH	0.019	-0.302	0.017	0.129	-0.064
Al-NaOH	-0.020	0.264	0.128	0.199	0.160
Ca-NaOH	0.106	-0.156	0.260	-0.002	0.150
gilvin-NaOH	-0.220	0.019	0.130	-0.079	-0.111
FNRP-HCl	0.191	0.146	-0.033	0.070	-0.107
FRP-HCl	0.203	0.120	0.074	0.164	0.040
TFP-HCl	0.202	0.136	0.024	0.122	-0.031
Fe-HCl	-0.051	-0.057	-0.353	0.138	-0.208
Mn-HCl	0.124	-0.222	0.194	0.047	-0.001
Al-HCl	0.174	0.120	0.097	0.235	0.101
Ca-HCl	0.217	-0.013	-0.076	0.226	-0.061
TFP-Ashed	0.141	-0.077	-0.208	-0.153	0.196
Fe-Ashed	-0.083	-0.145	0.225	0.328	0.003
Mn-Ashed	0.164	-0.124	-0.216	-0.184	-0.025
Al-Ashed	-0.140	-0.051	0.260	-0.034	-0.320
Ca-Ashed	0.162	0.161	-0.093	0.132	0.230

Principal Component Scores

Sample	SCORE1	SCORE2	SCORE3	SCORE4	SCORE5
Peat wet 3	-3.738	-4.650	2.823	2.182	0.081
Floc wet 3	4.962	-2.282	1.790	-1.459	1.390
Peat dry 3	-3.983	2.270	2.363	-2.128	-2.088
Floc dry 3	3.343	4.213	1.277	1.553	-0.119
Peat wet 6	-2.189	-1.617	-4.369	0.649	-0.996
Floc wet 6	4.191	-2.576	-1.694	-1.467	-0.809
Peat dry 6	-4.955	2.026	-1.303	-1.053	2.639
Floc dry 6	2.369	2.615	-0.887	1.723	-0.097

ANOSIM Analysis of Similarities

Similarity

Create triangular similarity/distance matrix

Sample selection: All
Variable selection: All

Parameters

Analyse between: Samples
Similarity measure: Euclidean distance
Standardise: Yes
Transform: None

Two-way crossed Analysis

Factor: Sediment
Peat
Floc

Factor: Treatment
Wet
Dry

Factor Groups

Sample	Sediment	Treatment
Peat wet 3	Peat	Wet
Peat wet 6	Peat	Wet
Peat dry 3	Peat	Dry
Peat dry 6	Peat	Dry
Floc wet 3	Floc	Wet
Floc wet 6	Floc	Wet
Floc dry 3	Floc	Dry
Floc dry 6	Floc	Dry

TESTS FOR DIFFERENCES BETWEEN Sediment GROUPS
(averaged across all Treatment groups)

Global Test

Sample statistic (Global R): 1.
Significance level of sample statistic: 11.1%
Number of permutations: 9 (All possible permutations)
Number of permuted statistics greater than or equal to
Global R: 1

TESTS FOR DIFFERENCES BETWEEN Treatment GROUPS
(averaged across all Sediment groups)

Global Test

Sample statistic (Global R): 0.5
Significance level of sample statistic: 22.2%
Number of permutations: 9 (All possible permutations)
Number of permuted statistics greater than or equal to
Global R: 2

Two-way crossed Analysis (using pseudo-reps)

Factor Values

Factor: Sediment
Peat
Floc

Factor: Treatment
wet
dry

TESTS FOR DIFFERENCES BETWEEN Sediment GROUPS
(averaged across all Treatment groups) (n=6)

Global Test

Sample statistic (Global R): 0.923
Significance level of sample statistic: 0.1%
Number of permutations: 999 (Random sample from 213444)
Number of permuted statistics greater than or equal to
Global R: 0

TESTS FOR DIFFERENCES BETWEEN Treatment GROUPS
(averaged across all Sediment groups) (n=6)

Global Test

Sample statistic (Global R): 0.544
Significance level of sample statistic: 0.1%
Number of permutations: 999 (Random sample from 213444)
Number of permuted statistics greater than or equal to
Global R: 0

PCA correlation matrices (Pearson coefficients) of phosphorus forms and co-extracted elements sequentially leached after the method of Ruttenberg (1992) (both sediment types and both treatments, n=8). These are the correlations on which the PCA analyses in Primer were based on.

Correlation Matrix $MgCl_2$ leach

		FRP	Fe	Mn	Ca	Al
Correlation	**FRP**	1.000				
	Fe	-.522				
	Mn	.257	-.136			
	Ca	.280	-.720	.262		
	Al	-.446	.510	-.082	-.354	
	S	.070	-.153	.812	.338	.298
Sig. (1-tailed)	**FRP**					
	Fe	.006				
	Mn	.124	.273			
	Ca	.103	.000	.120		
	Al	.019	.008	.359	.053	
	S	.378	.248	.000	.062	.089

Correlation Matrix NaOH

		FNP	FRP	Fe	Al
Correlation	**FRP**	.125			
	Fe	-.039	.376		
	Al	-.215	-.038	-.505	
	Gilvin	-.783	-.184	-.062	.169
Sig. (1-tailed)	**FRP**	.280			
	Fe	.427	.035		
	Al	.156	.429	.006	
	Gilvin	.000	.195	.386	.214

Correlation Matrix $NaHCO_3$ leach

		FNP	FRP	Fe	Mn	Al	Ca	S
Correlation	**FRP**	.636						
	Fe	-.398	-.274					
	Mn	.664	.291	-.199				
	Al	-.370	-.706	.622	.022			
	Ca	.191	-.212	.256	.690	.484		
	S	-.682	-.265	.710	-.571	.183	-.193	
	Gilvin	-.632	-.709	.541	-.235	.507	.296	.697
Sig. (1-tailed)								
	Fe	.027	.097					
	Mn	.000	.084	.176				
	Al	.038	.000	.001	.459			
	Ca	.186	.160	.114	.000	.008		
	S	.000	.105	.000	.002	.196	.183	
	Gilvin	.000	.000	.003	.135	.006	.080	.000

Correlation Matrix HCl leach

		FNP	FRP	Fe	Mn	A
Correlation	**FRP**	.598				
	Fe	-.089	-.321			
	Mn	.125	.245	-.331		
	Al	.733	.841	-.365	.223	
	Ca	.619	.711	.141	.341	
Sig. (1-tailed)	**FRP**	.001				
	Fe	.339	.063			
	Mn	.281	.125	.057		
	Al	.000	.000	.040	.147	
	Ca	.001	.000	.256	.052	

Correlation Matrix CDB leach

		TFP	Fe	Mn	Al	Ca
Correlation	**Fe**	-.382				
	Mn	.503	-.208			
	All	-.533	.856	-.455		
	Ca	-.419	.243	-.209	.541	
	Gilvin	-.316	.616	.221	.530	.543
Sig. (1-tailed)	**Fe**	.033				
	Mn	.006	.164			
	All	.004	.000	.013		
	Ca	.021	.126	.163	.003	
	Gilvin	.066	.001	.149	.004	.003

Correlation Matrix 'Ashed-aqua regia' leach

		TFP	Fe	Mn	Al
Correlation	**Fe**	-.488			
	Mn	.904	-.310		
	Al	.902	-.327	.881	
	Ca	.408	.642	-.270	-.203
Sig. (1-tailed)	**Fe**	.008			
	Mn	.000	.070		
	Al	.000	.060	.000	
	Ca	.024	.000	.101	.170

Appendix 5.3: Pearson's correlations between elements co-extracted in Lake Goollelal sediments (Sites and sediment types combined; n=4)

		FNP	FRP	TFP	Fe	Mn	Al	Ca	S
$MgCl_2$					**wet**				
Fe	Pearson Correlation		-0.787						
	Sig. (2-tailed)		0.213						
Mn	Pearson Correlation		0.989		-0.869				
	Sig. (2-tailed)		0.011*		0.131				
Al	Pearson Correlation		-0.545		-0.084	-0.419			
	Sig. (2-tailed)		0.455		0.916	0.581			
Ca	Pearson Correlation		0.580		-0.956	0.690	0.368		
	Sig. (2-tailed)		0.420		0.044*	0.310	0.632		
S	Pearson Correlation		0.690		-0.942	0.784	0.127	0.896	
	Sig. (2-tailed)		0.310		0.058	0.216	0.873	0.104	
$NaHCO_3$									
FRP	Pearson Correlation	0.931							
	Sig. (2-tailed)	0.069							
TFP	Pearson Correlation	0.974	0.989						
	Sig. (2-tailed)	0.026*	0.011*						
Fe	Pearson Correlation	-0.600	-0.668	-0.652					
	Sig. (2-tailed)	0.400	0.332	0.348					
Mn	Pearson Correlation	0.562	0.804	0.721	-0.348				
	Sig. (2-tailed)	0.438	0.196	0.279	0.652				
Al	Pearson Correlation	-0.923	-0.996	-0.984	0.605	-0.834			
	Sig. (2-tailed)	0.077	0.004**	0.016*	0.395	0.166			
Ca	Pearson Correlation	-0.428	-0.283	-0.345	0.790	0.256	0.205		
	Sig. (2-tailed)	0.572	0.717	0.655	0.210	0.744	0.795		
S	Pearson Correlation	-0.515	-0.546	-0.543	0.985	-0.183	0.475	0.870	
	Sig. (2-tailed)	0.485	0.454	0.457	0.015*	0.817	0.525	0.130	
Gilvin	Pearson Correlation	-0.714	-0.716	-0.727	0.979	-0.306	0.655	0.841	0.968
	Sig. (2-tailed)	0.286	0.284	0.273	0.021*	0.694	0.345	0.159	0.032*
CDB									
Fe	Pearson Correlation			-0.934					
	Sig. (2-tailed)			0.066					
Mn	Pearson Correlation			-0.104	-0.130				
	Sig. (2-tailed)			0.896	0.870				
Al	Pearson Correlation			-0.965	0.994	-0.036			
	Sig. (2-tailed)			0.035*	0.006**	0.964			
Ca	Pearson Correlation			-0.036	-0.306	0.844	-0.200		
	Sig. (2-tailed)			0.964	0.694	0.156	0.800		
Gilvin	Pearson Correlation			-0.805	0.622	0.674	0.700	0.521	
	Sig. (2-tailed)			0.195	0.378	0.326	0.300	0.479	
NaOH									
FRP	Pearson Correlation	-0.573							
	Sig. (2-tailed)	0.427							
TFP	Pearson Correlation	0.999	-0.547						
	Sig. (2-tailed)	0.001**	0.453						
Fe	Pearson Correlation	-0.718	-0.038	-0.735					
	Sig. (2-tailed)	0.282	0.962	0.265					
Mn	Pearson Correlation	-0.319	-0.176	-0.334	0.830				
	Sig. (2-tailed)	0.681	0.824	0.666	0.170				
Al	Pearson Correlation	-0.299	0.847	-0.272	-0.031	0.138			
	Sig. (2-tailed)	0.701	0.153	0.728	0.969	0.862			
Ca	Pearson Correlation	0.528	0.194	0.548	-0.457	0.065	0.627		
	Sig. (2-tailed)	0.472	0.806	0.452	0.543	0.935	0.373		
Gilvin	Pearson Correlation	-0.870	0.647	-0.864	0.722	0.584	0.630	-0.077	
	Sig. (2-tailed)	0.130	0.353	0.136	0.278	0.416	0.370	0.923	
HCl									
FRP	Pearson Correlation	0.685							
	Sig. (2-tailed)	0.315							
TFP	Pearson Correlation	0.917	0.918						
	Sig. (2-tailed)	0.083	0.082						
Fe	Pearson Correlation	0.050	-0.618	-0.310					
	Sig. (2-tailed)	0.950	0.382	0.690					
Mn	Pearson Correlation	-0.157	0.488	0.181	-0.985				
	Sig. (2-tailed)	0.843	0.512	0.819	0.015*				
Al	Pearson Correlation	0.446	0.901	0.735	-0.871	0.800			
	Sig. (2-tailed)	0.554	0.099	0.265	0.129	0.200			
Ca	Pearson Correlation	0.954	0.650	0.874	-0.081	0.012	0.531		
	Sig. (2-tailed)	0.046*	0.350	0.126	0.919	0.988	0.469		
Ashed									
Fe	Pearson Correlation			-0.931					
	Sig. (2-tailed)			0.069					
Mn	Pearson Correlation			0.754	-0.904				
	Sig. (2-tailed)			0.246	0.096				
Al	Pearson Correlation			-0.931	0.999	-0.920			
	Sig. (2-tailed)			0.069	0.001**	0.080			
Ca	Pearson Correlation			0.960	-0.938	0.880	-0.950		
	Sig. (2-tailed)			0.04*	0.062	0.120	0.05*		

		FNP	FRP	TFP	Fe	Mn	Al	Ca	S	
$MgCl_2$					**dry**					
Fe	Pearson Correlation		-0.479							
	Sig. (2-tailed)		0.521							
Mn	Pearson Correlation		0.772		-0.893					
	Sig. (2-tailed)		0.228		0.107					
Al	Pearson Correlation		-0.491		0.988	-0.856				
	Sig. (2-tailed)		0.509		0.012*	0.144				
Ca	Pearson Correlation		0.145		-0.868	0.739	-0.790			
	Sig. (2-tailed)		0.855		0.132	0.261	0.210			
S	Pearson Correlation		0.364		-0.682	0.786	-0.560	0.863		
	Sig. (2-tailed)		0.636		0.318	0.214	0.440	0.137		
$NaHCO_3$										
FRP	Pearson Correlation	0.908								
	Sig. (2-tailed)	0.092								
TFP	Pearson Correlation	0.934	0.998							
	Sig. (2-tailed)	0.066	0.002**							
Fe	Pearson Correlation	-0.406	-0.121	-0.167						
	Sig. (2-tailed)	0.594	0.879	0.833						
Mn	Pearson Correlation	-0.925	-0.934	-0.945	0.030					
	Sig. (2-tailed)	0.075	0.066	0.055	0.970					
Al	Pearson Correlation	-0.737	-0.605	-0.634	0.848	0.446				
	Sig. (2-tailed)	0.263	0.395	0.366	0.152	0.554				
Ca	Pearson Correlation	-0.982	-0.872	-0.900	0.553	0.843	0.850			
	Sig. (2-tailed)	0.018*	0.128	0.100	0.447	0.157	0.150			
S	Pearson Correlation	-0.682	-0.342	-0.400	0.884	0.388	0.806	0.758		
	Sig. (2-tailed)	0.318	0.658	0.600	0.116	0.612	0.194	0.242		
Gilvin	Pearson Correlation	-0.988	-0.943	-0.961	0.260	0.972	0.639	0.945	0.568	
	Sig. (2-tailed)	0.012*	0.057	0.039*	0.740	0.028*	0.361	0.055	0.432	
CDB										
Fe	Pearson Correlation			0.059						
	Sig. (2-tailed)			0.941						
Mn	Pearson Correlation			0.378	-0.902					
	Sig. (2-tailed)			0.622	0.098					
Al	Pearson Correlation			0.005	0.993	-0.920				
	Sig. (2-tailed)			0.995	0.007**	0.080				
Ca	Pearson Correlation			-0.628	0.722	-0.943	0.770			
	Sig. (2-tailed)			0.372	0.278	0.057	0.230			
Gilvin	Pearson Correlation			-0.724	0.646	-0.913	0.683	0.980		
	Sig. (2-tailed)			0.276	0.354	0.087	0.317	0.020		
NaOH										
FRP	Pearson Correlation	0.762								
	Sig. (2-tailed)	0.238								
TFP	Pearson Correlation	1.000	0.779							
	Sig. (2-tailed)	0.000**	0.221							
Fe	Pearson Correlation	0.809	0.990	0.824						
	Sig. (2-tailed)	0.191	0.001**	0.176						
Mn	Pearson Correlation	0.855	0.983	0.868	0.996					
	Sig. (2-tailed)	0.145	0.017*	0.132	0.004**					
Al	Pearson Correlation	0.497	-0.175	0.475	-0.075	-0.003				
	Sig. (2-tailed)	0.503	0.825	0.525	0.925	0.997				
Ca	Pearson Correlation	0.680	0.336	0.672	0.309	0.382	0.486			
	Sig. (2-tailed)	0.320	0.664	0.328	0.691	0.618	0.514			
Gilvin	Pearson Correlation	-0.921	-0.703	-0.920	-0.791	-0.819	-0.510	-0.361		
	Sig. (2-tailed)	0.079	0.297	0.080	0.209	0.181	0.490	0.639		
HCl										
FRP	Pearson Correlation	0.976								
	Sig. (2-tailed)	0.024*								
TFP	Pearson Correlation	0.993	0.995							
	Sig. (2-tailed)	0.007**	0.005**							
Fe	Pearson Correlation	-0.334	-0.121	-0.222						
	Sig. (2-tailed)	0.666	0.879	0.778						
Mn	Pearson Correlation	0.918	0.869	0.897	-0.417					
	Sig. (2-tailed)	0.082	0.131	0.103	0.583					
Al	Pearson Correlation	0.972	0.974	0.979	-0.223	0.802				
	Sig. (2-tailed)	0.028	0.026*	0.021*	0.777	0.198				
Ca	Pearson Correlation	0.878	0.961	0.928	0.157	0.751	0.905			
	Sig. (2-tailed)	0.122	0.039*	0.072	0.843	0.249	0.095			
Ashed										
Fe	Pearson Correlation			-0.045						
	Sig. (2-tailed)			0.955						
Mn	Pearson Correlation			0.857	0.327					
	Sig. (2-tailed)			0.143	0.673					
Al	Pearson Correlation			-0.991	-0.068	-0.863				
	Sig. (2-tailed)			0.009**	0.932	0.137				
Ca	Pearson Correlation			0.757	0.576	0.790	-0.837			
	Sig. (2-tailed)			0.243	0.424	0.210	0.163			

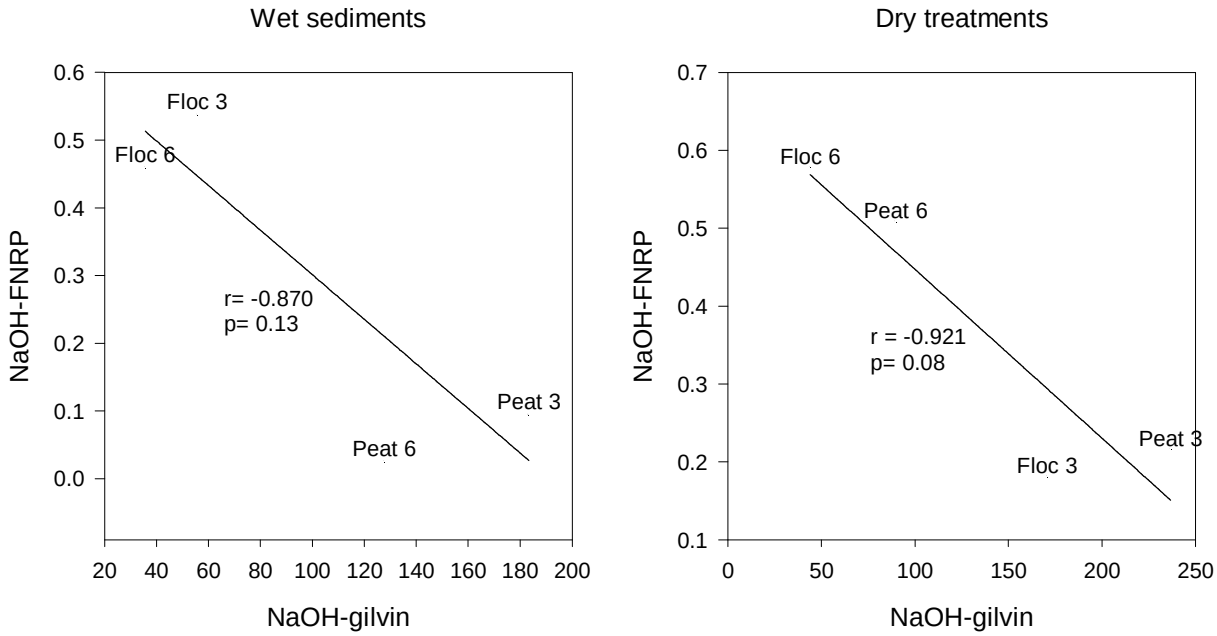


Figure 1: Scatter graphs of gilvin against FNRP (filterable non-reactive phosphorus) in the NaOH leaches of wet and dry Lake Goollelal sediments.

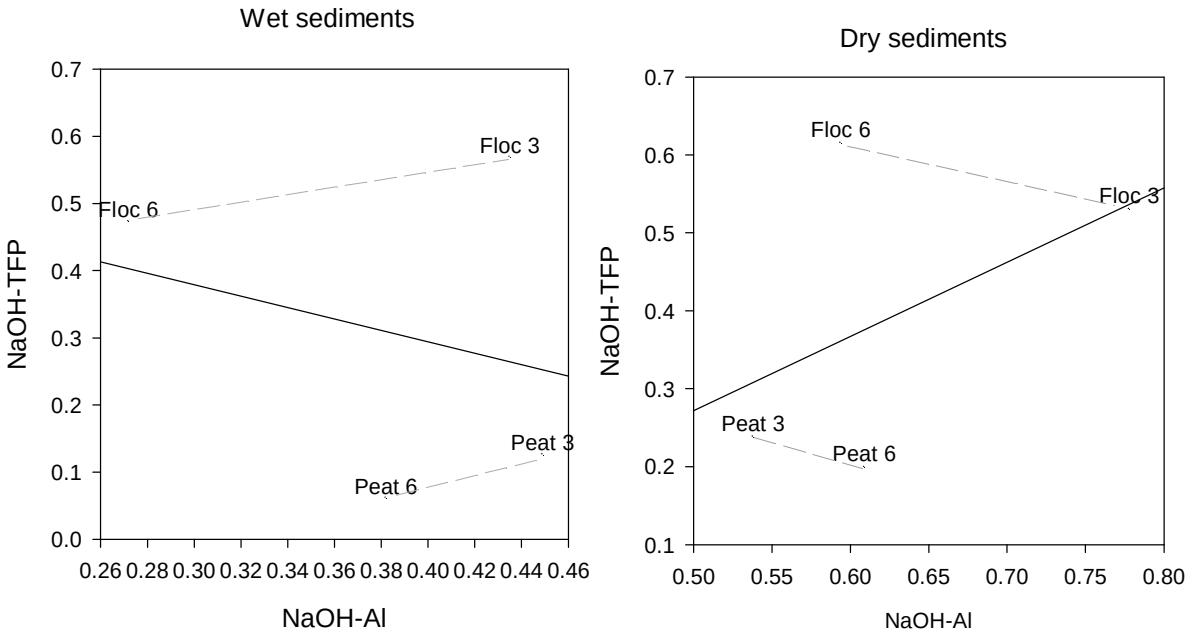


Figure 2: Scatter graphs of Al against TFP (total filterable phosphorus) in the NaOH leaches of wet and dry Lake Goollelal sediments. There were no significant correlations when sediment types were combined, but within the sediment types high Al was associated with high TFP in both the wet peat and the wet floc. In the dried treatments, low Al was associated with high TFP.

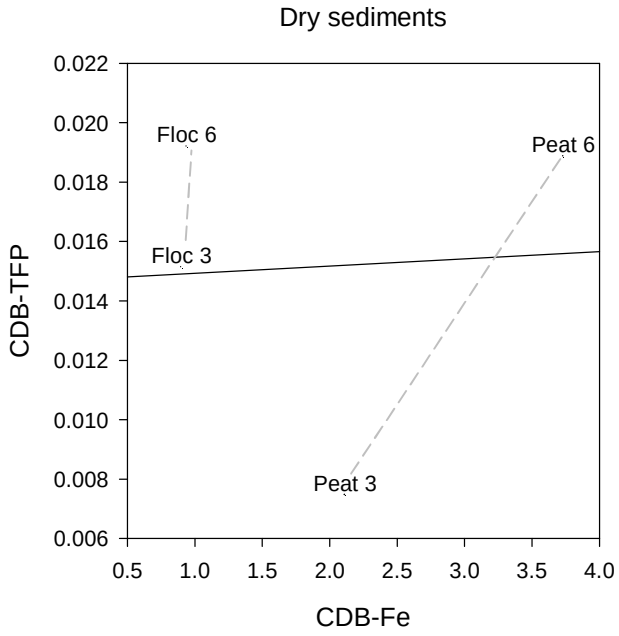
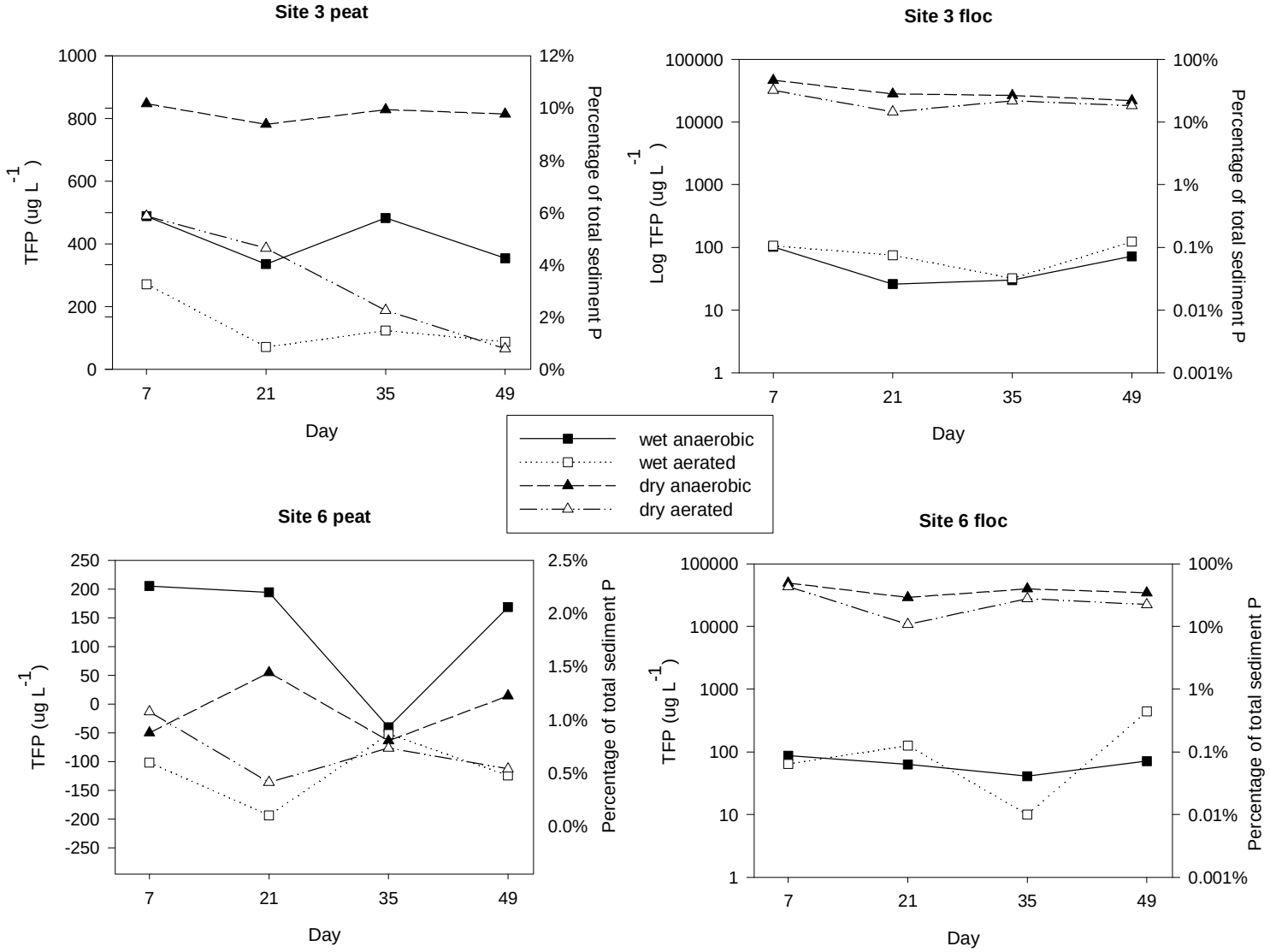


Figure 3: Scatter graphs of Fe against TFP (total filterable phosphorus) in the CDB leaches of dry Lake Goollelal sediments. There were no significant correlations when sediment types were combined, but within the sediment types high Fe was associated with high TFP in the dry peat, but not in the dry.

Appendix 5.4: TFP (total filterable phosphorus) release over 49 days of incubation, Sites 3 and 6, wet and dried/rewet peat and floc sediments from Lake Goollelal. These graphs were produced from data in Chapter 4.



Appendix 5.5

Efficiency of multiple $MgCl_2$, $NaHCO_3$, CDB and NaOH extractions

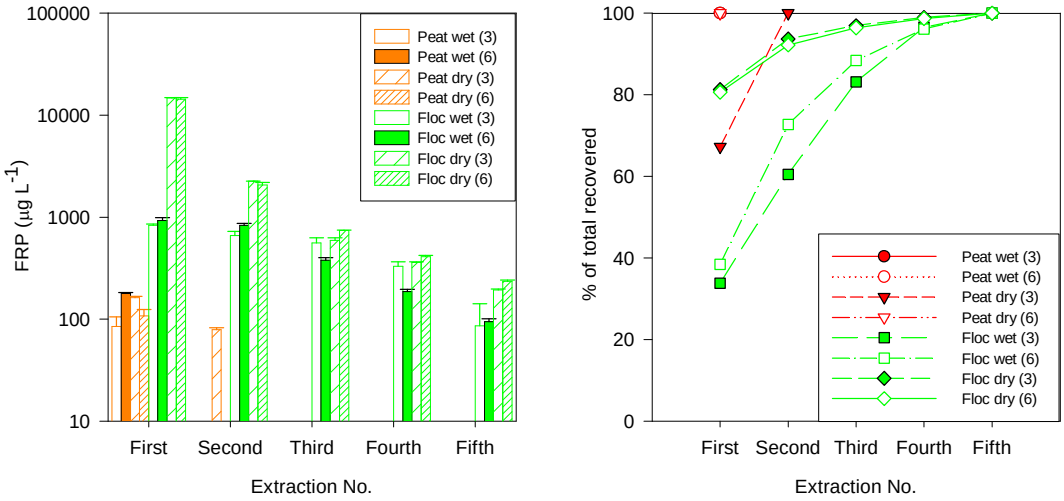


Figure 1: Concentration of (log-) FRP (a) and percentage of total FRP (b) recovered in individual **$MgCl_2$** extracts of Lake Goollelal sediments. Error bars are standard errors (n=3).

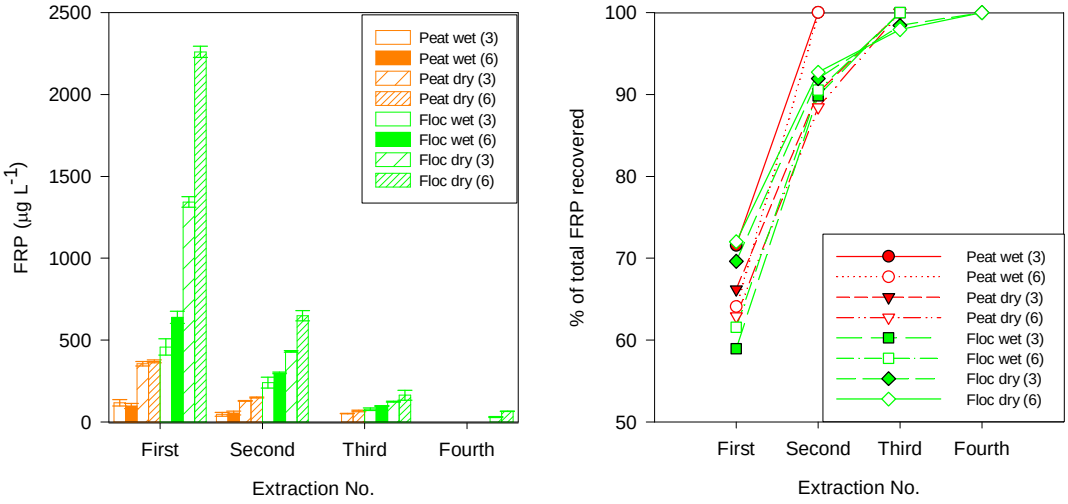


Figure 2: Concentration of FRP (a) and percentage of total FRP (b) recovered in individual **$NaHCO_3$** extracts of Lake Goollelal sediments. Error bars are standard errors (n=3).

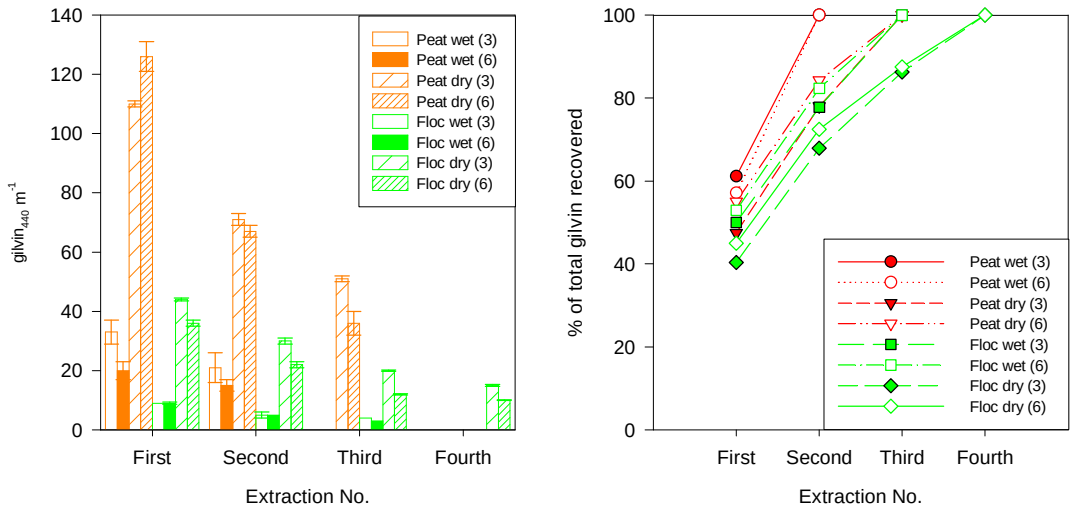


Figure 3: Gilvin$_{440}$ g^{-1} sediment l^{-1} (a) and percentage of total gilvin (b) recovered in individual **$NaHCO_3$** extracts of Lake Goollelal sediments. Error bars are standard errors (n=3).

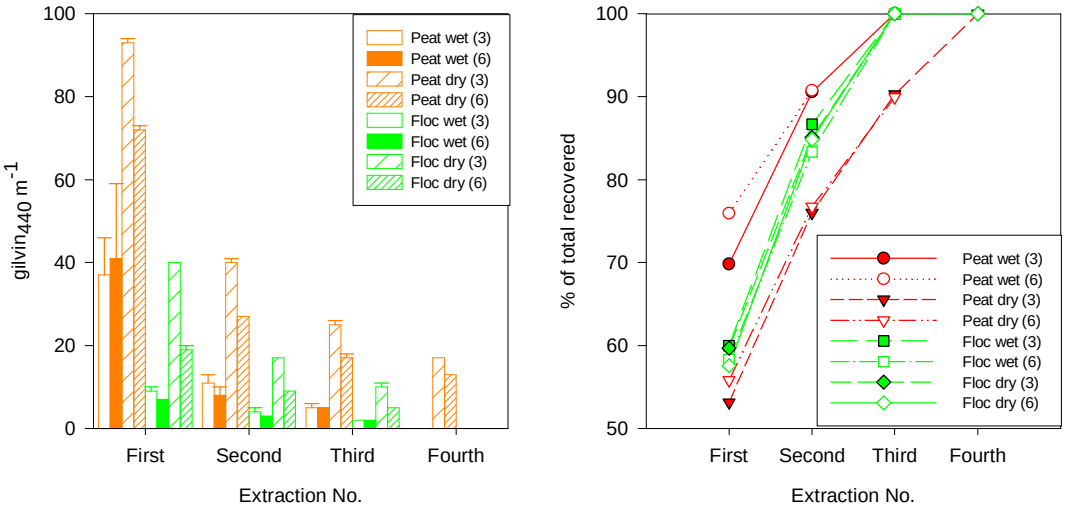


Figure 4: Gilvin$_{440}$ g^{-1} sediment l^{-1} (a) and percentage of total gilvin (b) recovered in individual **CDB** extracts of Lake Goollelal sediments. Error bars are standard errors (n=3).

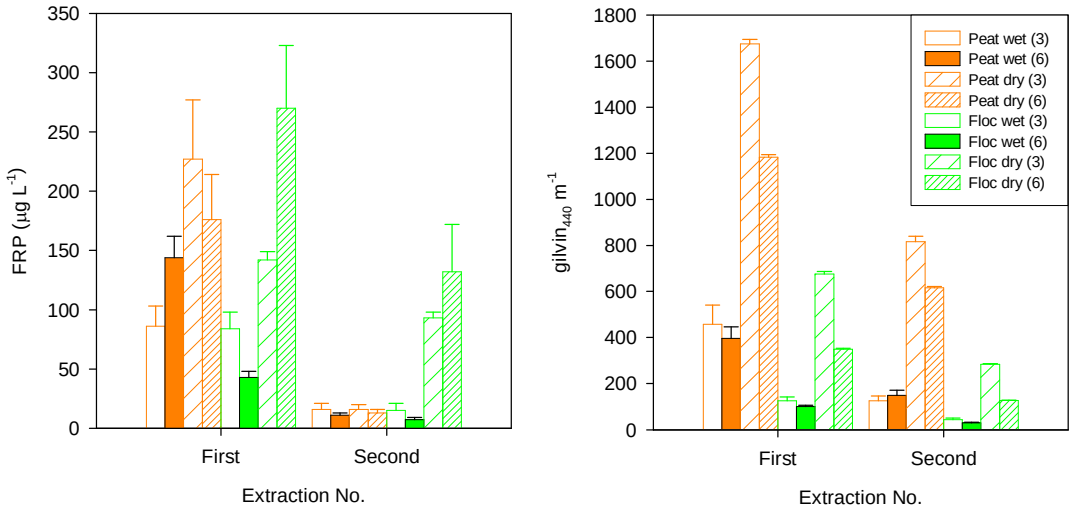


Figure 5: Concentration of FRP (a) and gilvin$_{440}$ content (b) in individual NaOH extracts of Lake Goollelal sediments. Error bars are standard errors (n=3).

Chapter 6

6.1 Mass balance of Lake Goollelal extraction data (Tables 1 – 7)

6.2 Pearson correlation coefficients (and significance levels) of elements extracted sequentially after the method of Hall (1996) (both sediment types and both treatments, n=8).

6.3 PRIMER raw results for elemental extractions

Appendix 6.1: Mass balances of P fractionation data

Table 1: Lake Goollelal sediment iron extraction data (mg g^{-1} (standard error); n=3) and respective percentages of total extractable iron for 2 sites. The last column shows the percentages of total iron extracted by the scheme of the total sediment iron as determined on a sediment sub-sample by X-Ray Fluorescence (XRF) analysis.

Site 3 (mg Fe/g sediment)	NaOAc	Pyro-P	0.25 M NH_2.OH.HCl	1 M NH_2.OH.HCl	$KClO_3$	Residual	Total extractable	Total Fe
Peat dry	0.03 (0.003)	1.33 (0.022)	1.77 (0.049)	0.19 (0.006)	20.64(0.217)	0.22 (0.001)	24.18 (0.278)	27.80
Peat wet	0.82 (0.103)	3.43 (0.177)	1.55 (0.129)	0.24 (0.029)	21.42 (0.934)	0.24 (0.015)	27.70 (1.388)	
Floc dry	0.05 (0.001)	1.23 (0.008)	0.92 (0.014)	0.13 (0.005)	25.28 (0.327)	0.43 (0.004)	28.03 (0.359)	29.70
Floc wet	1.60 (0.046)	0.76 (0.034)	0.56 (0.035)	0.12 (0.014)	20.90 (0.613)	0.36 (0.013)	24.29 (0.756)	

Mean percentage of total extractable								Percentage of total sediment Fe extracted
Peat dry	0.11	5.50	7.33	0.80	85.38	0.89	100	82.11
Peat wet	2.97	12.38	5.60	0.85	77.33	0.87	100	96.84
Floc dry	0.16	4.40	3.29	0.46	90.16	1.53	100	94.39
Floc wet	6.59	3.13	2.30	0.47	86.02	1.48	100	81.79

Site 6 (mg Fe/g sediment)	NaOAc	Pyro-P	0.25 M NH_2.OH.HCl	1 M NH_2.OH.HCl	$KClO_3$	Residual	Total extractable	Total Fe
Peat dry	2.10 (0.017)	6.21 (0.076)	3.28 (0.060)	0.46 (0.015)	26.17 (0.397)	0.25 (0.012)	38.47 (0.577)	58.60
Peat wet	3.39 (0.243)	5.79 (0.147)	3.91 (0.085)	0.58 (0.035)	38.70 (1.072)	0.30 (0.011)	52.66 (1.592)	
Floc dry	0.21 (0.007)	2.26 (0.033)	0.84 (0.014)	0.15 (0.003)	57.26 (0.240)	0.37 (0.014)	61.09 (0.311)	64.90
Floc wet	3.10 (0.169)	0.83 (0.056)	0.57 (0.011)	0.16 (0.011)	47.60 (3.122)	0.33 (0.031)	52.58 (3.398)	

Mean percentage of total extractable								Percentage of total sediment Fe extracted
Peat dry	5.46	16.15	8.51	1.20	68.02	0.65	100	65.65
Peat wet	6.44	10.99	7.42	1.11	73.48	0.56	100	89.87
Floc dry	0.34	3.70	1.38	0.24	93.72	0.61	100	94.13
Floc wet	5.89	1.58	1.08	0.30	90.53	0.62	100	81.02

Table 2: Lake Goollelal sediment manganese extraction data (mg g^{-1} (standard error); n=3) and respective percentages of total extractable iron for 2 sites. The last column shows the percentages of total manganese extracted by the scheme of the total sediment manganese as determined on a sediment sub-sample after acid digestion (aqua regia) and analysis by inductively coupled plasma spectroscopy (ICP).

Site 3 (mg Mn/g sediment)	NaOAc	Pyro-P	0.25 M NH_2.OH.HCl	1 M NH_2.OH.HCl	$KClO_3$	Residual	Total extractable	Total Mn
Peat dry	0.018 (0.0002)	0.002 (0.0002)	0.003 (0.0002)	0.001 (0.0001)	0.005 (0.0001)	0.002 (0.0001)	0.032 (0.0008)	0.033
Peat wet	0.015 (0.0002)	0.001 (0.0002)	0.003 (0.0001)	0.001 (0.0003)	0.006 (0.0006)	0.002 (0.0000)	0.028 (0.0014)	
Floc dry	0.016 (0.0002)	0.002 (0.0000)	0.002 (0.0001)	0.001 (0.0000)	0.043 (0.0006)	0.004 (0.0000)	0.069 (0.0009)	0.089
Floc wet	0.017 (0.0004)	0.002(0.0001)	0.002 (0.0000)	0.001 (0.0001)	0.040 (0.0013)	0.004 (0.0001)	0.065 (0.0021)	

Mean percentage of total extractable								Percentage of total sediment Mn extracted
Peat dry	57.90	7.15	10.75	2.16	16.73	5.31	100	96.36
Peat wet	53.94	4.49	10.13	3.44	21.11	6.88	100	84.88
Floc dry	23.71	3.25	3.29	1.06	62.86	5.85	100	77.43
Floc wet	25.53	2.71	3.04	1.08	61.98	5.66	100	72.72

Site 6 (mg Mn/g sediment)	NaOAc	Pyro-P	0.25 M NH_2.OH.HCl	1 M NH_2.OH.HCl	$KClO_3$	Residual	Total extractable	Total Mn
Peat dry	0.013 (0.0001)	0.001 (0.0001)	0.002 (0.0000)	0.000 (0.0000)	0.002 (0.0001)	0.0015 (0.0002)	0.020 (0.0006)	0.021
Peat wet	0.010 (0.0004)	0.000 (0.0000)	0.001 (0.0000)	0.0004 (0.0001)	0.004 (0.0001)	0.0018 (0.0001)	0.017 (0.0007)	
Floc dry	0.014 (0.0001)	0.001 (0.0001)	0.0015 (0.0000)	0.0005 (0.0001)	0.031 (0.0001)	0.003 (0.0000)	0.051 (0.0005)	0.050
Floc wet	0.013 (0.008)	0.001 (0.0000)	0.001 (0.0001)	0.000 (0.0000)	0.031 (0.0023)	0.003 (0.0002)	0.049 (0.0035)	

Mean percentage of total extractable								Percentage of total sediment Mn extracted
Peat dry	66.61	3.06	10.45	0.94	11.16	7.78	100	94.33
Peat wet	59.40	0.06	8.14	0.02	21.54	10.83	100	80.26
Floc dry	27.50	2.09	3.02	1.01	61.31	5.06	100	102.72
Floc wet	25.72	2.03	2.71	0.72	63.67	5.15	100	98.77

Table 3: Lake Goollelal sediment aluminium extraction data (mg g^{-1} (standard error); n=3) and respective percentages of total extractable aluminium for 2 sites. The last column shows the percentages of total aluminium extracted by the scheme of the total sediment aluminium as determined on a sediment sub-sample by X-Ray Fluorescence (XRF) analysis.

Site 3 (mg Al/g sediment)	NaOAc	Pyro-P	0.25 M NH_2.OH.HCl	1 M NH_2.OH.HCl	$KClO_3$	Residual	Total extractable	Total Al
Peat dry	0.047 (0.0007)	0.703 (0.0040)	0.379 (0.0075)	0.237 (0.0058)	0.157 (0.0030)	1.46 (0.0162)	2.986 (0.0373)	3.200
Peat wet	0.130 (0.0090)	0.852 (0.1187)	0.449 (0.0303)	0.310 (0.0211)	0.142 (0.0032)	1.41 (0.1349)	3.29 (0.3172)	
Floc dry	0.058 (0.0010)	0.451 (0.0046)	0.644 (0.0149)	0.416 (0.0072)	0.243 (0.0038)	3.125 (0.0534)	4.937 (0.0848)	5.900
Floc wet	0.029 (0.0041)	0.449 (0.0242)	0.668 (0.0134)	0.501 (0.0258)	0.217 (0.0117)	2.750 (0.1024)	4.614 (0.1815)	

Mean percentage of total extractable								Percentage of total sediment Al extracted
Peat dry	1.59	23.54	12.70	7.95	5.27	48.94	100	93.31
Peat wet	3.94	25.88	13.63	9.41	4.30	42.84	100	102.81
Floc dry	1.18	9.14	13.05	8.42	4.93	63.30	100	83.68
Floc wet	0.63	9.73	14.47	10.87	4.70	59.60	100	78.21

Site 6 (mg Al/g sediment)	NaOAc	Pyro-P	0.25 M NH_2.OH.HCl	1 M NH_2.OH.HCl	$KClO_3$	Residual	Total extractable	Total Al
Peat dry	0.386 (0.0018)	0.867 (0.0070)	0.343 (0.0048)	0.229 (0.0117)	0.147 (0.0029)	1.417 (0.1233)	3.389 (0.1514)	4.100
Peat wet	0.299 (0.0136)	0.918 (0.0456)	0.510 (0.0191)	0.299 (0.0201)	0.114 (0.0155)	1.491 (0.0979)	3.632 (0.2118)	
Floc dry	0.844 (0.0323)	0.304 (0.0050)	0.458 (0.0078)	0.299 (0.0046)	0.150 (0.0032)	1.979 (0.0592)	4.034 (0.1121)	4.600
Floc wet	0.179 (0.0261)	0.395 (0.0305)	0.509 (0.0433)	0.390 (0.0204)	0.157 (0.0084)	2.01 (0.1576)	3.643 (0.2863)	

Mean percentage of total extractable								Percentage of total sediment Al extracted
Peat dry	11.39	25.57	10.13	6.75	4.35	41.80	100	82.65
Peat wet	8.23	25.29	14.04	8.24	3.15	41.05	100	88.58
Floc dry	20.92	7.54	11.36	7.42	3.72	49.05	100	87.70
Floc wet	4.92	10.86	13.97	10.72	4.32	55.22	100	79.19

Table 4: Lake Goollelal sediment calcium extraction data (mg g^{-1} (standard error); n=3) and respective percentages of total extractable calcium for 2 sites. The last column shows the percentages of total calcium extracted by the scheme of the total sediment calcium as determined on a sediment sub-sample by X-Ray Fluorescence (XRF) analysis.

Site 3 (mg Ca/g sediment)	NaOAc	Pyro-P	0.25 M NH_2.OH.HCl	1 M NH_2.OH.HCl	$KClO_3$	Residual	Total extractable	Total Ca
Peat dry	15.41 (0.173)	2.07 (0.072)	0.12 (0.018)	0.08 (0.008)	0.15 (0.005)	0.17 (0.019)	18.00 (0.295)	20
Peat wet	12.51 (0.367)	2.62 (0.059)	0.57 (0.237)	0.16 (0.044)	0.54 (0.218)	0.18 (0.009)	16.58 (0.934)	
Floc dry	14.04 (0.209)	1.52 (0.065)	0.09 (0.017)	0.04 (0.006)	0.11 (0.027)	0.18 (0.009)	15.97 (0.333)	17
Floc wet	12.18 (0.283)	2.08 (0.143)	0.28 (0.030)	0.12 (0.015)	0.65 (0.172)	0.30 (0.029)	15.60 (0.672)	
Mean percentage of total extractable								**Percentage of total sediment Ca extracted**
Peat dry	85.60	11.52	0.65	0.45	0.81	0.96	100	91.86
Peat wet	75.46	15.78	3.45	0.98	3.26	1.07	100	84.59
Floc dry	87.87	9.48	0.55	0.25	0.71	1.13	100	94.53
Floc wet	78.10	13.31	1.77	0.76	4.14	1.92	100	92.31

Site 6 (mg Ca/g sediment)	NaOAc	Pyro-P	0.25 M NH_2.OH.HCl	1 M NH_2.OH.HCl	$KClO_3$	Residual	Total extractable	Total Ca
Peat dry	7.94 (0.021)	0.89 (0.048)	0.02 (0.007)	0.05(0.014)	0.09 (0.030)	0.14 (0.027)	9.12 (0.148)	8
Peat wet	5.96 (0.165)	0.97 (0.165)	0.08 (0.071)	0.07 (0.021)	0.32 (0.028)	0.35 (0.202)	7.76 (0.722)	
Floc dry	8.27 (0.060)	0.96 (0.035)	0.06 (0.012)	0.04 (0.014)	0.05 (0.034)	0.13 (0.008)	9.49 (0.164)	12
Floc wet	7.64 (0.451)	1.36 (0.034)	0.21 (0.048)	0.17 (0.105)	0.21 (0.066)	0.18 (0.018)	9.78 (0.722)	
Mean percentage of total extractable								**Percentage of total sediment Ca extracted**
Peat dry	87.02	9.71	0.23	0.50	1.02	1.53	100.00	120.06
Peat wet	76.88	12.53	1.06	0.90	4.10	4.53	100.00	102.07
Floc dry	87.10	10.09	0.61	0.37	0.47	1.35	100.00	79.76
Floc wet	78.10	13.94	2.12	1.78	2.18	1.88	100.00	82.19

Table 5: Lake Goollelal sediment phosphorus extraction data (mg g^{-1} (standard error); n=3) and respective percentages of total extractable phosphorus for 2 sites. The last column shows the percentages of total phosphorus extracted by the scheme of the total sediment phosphorus as determined on a sediment sub-sample by X-Ray Fluorescence (XRF) analysis. Note: only the sodium acetate extraction data were used in the study because phosphorus was added in the seconded leach (pyro-phosphate).

Site 3 (mg P/g sediment)	NaOAc	Pyro-P	0.25 M NH_2.OH.HCl	1 M NH_2.OH.HCl	$KClO_3$	Residual	Total extractable	Total P
Peat dry	0.08 (0.013)	79.41	2.91	0.19	0.09	0.06	82.73	0.47
Peat wet	0.06 (0.024)	232.42	17.90	1.07	0.07	0.05	251.58	
Floc dry	1.79 (0.041)	131.15	3.65	0.33	0.14	0.10	137.16	3.31
Floc wet	1.53 (0.035)	307.52	17.98	1.14	0.11	0.10	328.37	
Mean percentage of total extractable								**Percentage of total sediment P extracted**
Peat dry	0.10	95.98	3.51	0.23	0.11	0.07	100	17602.90
Peat wet	0.03	92.38	7.11	0.43	0.03	0.02	100	53528.60
Floc dry	1.30	95.62	2.66	0.24	0.10	0.07	100	4143.75
Floc wet	0.47	93.65	5.48	0.35	0.03	0.03	100	9920.67

Site 6 (mg P/g sediment)	NaOAc	Pyro-P	0.25 M NH_2.OH.HCl	1 M NH_2.OH.HCl	$KClO_3$	Residual	Total extractable	Total P
Peat dry	0.08 (0.012)	55.62	1.73	0.15	0.06	0.06	57.70	0.45
Peat wet	0.06 (0.017)	259.57	17.90	0.91	0.06	0.06	278.57	
Floc dry	1.71 (0.038)	113.82	3.24	0.31	0.09	0.07	119.24	3.35
Floc wet	1.41 (0.132)	237.48	12.74	0.82	0.08	0.06	252.59	
Mean percentage of total extractable								**Percentage of total sediment P extracted**
Peat dry	0.14	96.40	2.99	0.25	0.11	0.10	100	12822.06
Peat wet	0.02	93.18	6.43	0.33	0.02	0.02	100	61904.15
Floc dry	1.44	95.45	2.72	0.26	0.07	0.06	100	3559.50
Floc wet	0.56	94.02	5.04	0.32	0.03	0.02	100	7539.95

Table 6: Lake Goollelal sediment sulfur extraction data (mg g^{-1} (standard error); n=3) and respective percentages of total extractable sulfur for 2 sites. The last column shows the percentages of total sulfur extracted by the scheme of the total sediment sulfur as determined on a sediment sub-sample on a Leico total sulfur analyser.

Site 3 (mg S/g sediment)	NaOAc	Pyro-P	0.25 M NH_2.OH.HCl	1 M NH_2.OH.HCl	$KClO_3$	Residual	Total extractable	Total S
Peat dry	1.88 (0.027)	2.46 (0.049)	1.74 (0.817)	3.33 (0.122)	30.05 (0.396)	2.52 (0.027)	41.97 (1.438)	51.20
Peat wet	4.36 (0.172)	1.89 (0.171)	0.66 (0.343)	2.83 (0.208)	30.13 (1.641)	2.43 (0.120)	42.30 (2.655)	
Floc dry	1.61 (0.034)	2.37 (0.119)	0.73 (0.006)	3.26 (0.028)	33.20 (0.309)	2.01 (0.029)	43.19 (0.525)	52.60
Floc wet	1.96 (0.239)	1.77 (0.106)	0.49 (0.122)	3.29 (0.121)	27.37 (0.836)	1.68 (0.043)	36.57 (1.467)	

Mean percentage of total extractable								Percentage of total sediment S extracted
Peat dry	4.48	5.85	4.14	7.94	71.59	5.99	100	81.97
Peat wet	11.08	4.82	1.68	7.21	69.03	6.18	100	76.77
Floc dry	3.73	5.49	1.69	7.55	76.88	4.66	100	82.11
Floc wet	5.37	4.85	1.35	9.00	74.84	4.60	100	69.53

Site 6 (mg S/g sediment)	NaOAc	Pyro-P	0.25 M NH_2.OH.HCl	1 M NH_2.OH.HCl	$KClO_3$	Residual	Total extractable	Total S
Peat dry	1.88 (0.021)	2.10 (0.136)	1.05 (0.111)	3.61 (0.049)	35.11 (0.569)	2.73 (0.083)	46.49 (0.970)	61.30
Peat wet	0.59 (0.139)	1.46 (0.199)	0.48 (0.043)	3.36 (0.024)	47.44 (1.499)	2.70 (0.061)	56.03 (1.965)	
Floc dry	0.98 (0.015)	2.21 (0.079)	0.69 (0.027)	3.09 (0.059)	66.11 (0.160)	1.55 (0.060)	74.63 (0.399)	75.70
Floc wet	0.56 (0.163)	1.83 (0.083)	0.43 (0.032)	3.34 (0.182)	55.09 (3.598)	1.47 (0.101)	62.71 (4.159)	

Mean percentage of total extractable								Percentage of total sediment S extracted
Peat dry	4.05	4.52	2.27	7.77	75.53	5.87	100	75.84
Peat wet	1.06	2.61	0.85	5.99	84.67	4.82	100	91.41
Floc dry	1.31	2.96	0.93	4.14	88.58	2.08	100	98.59
Floc wet	0.89	2.92	0.69	5.32	87.84	2.34	100	82.85

Table 7: Lake Goollelal sediment silicon extraction data (mg g^{-1} (standard error); n=3) and respective percentages of total extractable silicon for 2 sites. The last column shows the percentages of total silicon extracted by the scheme of the total sediment silicon as determined on a sediment sub-sample by X-Ray Fluorescence (XRF) analysis.

Site 3 (mg Si/g sediment)	NaOAc	Pyro-P	0.25 M NH_2.OH.HCl	1 M NH_2.OH.HCl	$KClO_3$	Residual	Total extractable	Total Si
Peat dry	0.09 (0.003)	0.97 (0.031)	0.23 (0.010)	0.35 (0.034)	0.34 (0.014)	0.03 (0.013)	2.01 (0.105)	39.00
Peat wet	0.25 (0.031)	1.20 (0.038)	0.38 (0.037)	0.36 (0.052)	0.31 (0.018)	0 (0)	2.502 (0.176)	
Floc dry	0.11 (0.006)	1.63 (0.013)	0.48 (0.009)	0.67 (0.001)	0.63 (0.017)	0.03 (0.005)	3.56 (0.051)	57.90
Floc wet	0.31 (0.007)	2.65 (0.111)	0.71 (0.015)	0.65 (0.028)	0.54 (0.028)	0.01 (0.006)	4.86 (0.194)	

Mean percentage of total extractable								Percentage of total sediment Si extracted
Peat dry	4.69	48.28	11.53	17.32	16.89	1.29	100	5.16
Peat wet	10.18	48.03	15.12	14.21	12.45	0.00	100	6.42
Floc dry	3.01	45.91	13.58	18.94	17.60	0.94	100	6.15
Floc wet	6.35	54.47	14.59	13.29	11.17	0.13	100	8.39

Site 6 (mg Si/g sediment)	NaOAc	Pyro-P	0.25 M NH_2.OH.HCl	1 M NH_2.OH.HCl	$KClO_3$	Residual	Total extractable	Total Si
Peat dry	0.10 (0.006)	0.386 (0.027)	0.22 (0.003)	0.30 (0.006)	0.27 (0.005)	0 (0)	1.28 (0.049)	49.00
Peat wet	0.12 (0.007)	1.21 (0.103)	0.44 (0.025)	0.37 (0.025)	0.33 (0.025)	0 (0)	2.46 (0.185)	
Floc dry	0.12 (0.010)	1.98 (0.086)	0.45 (0.005)	0.55 (0.011)	0.61(0.014)	0.02 (0.008)	3.73 (0.134)	71.10
Floc wet	0.22 (0.005)	3.39 (0.123)	0.68 (0.053)	0.57 (0.043)	0.67 (0.041)	0.00 (0.002)	5.54 (0.268)	

Mean percentage of total extractable								Percentage of total sediment Si extracted
Peat dry	7.80	30.20	17.37	23.56	21.06	0.00	100	2.61
Peat wet	4.70	49.02	17.86	15.04	13.38	0.00	100	5.03
Floc dry	3.16	53.04	12.01	14.86	16.45	0.48	100	5.25
Floc wet	4.02	61.29	12.25	10.32	12.07	0.04	100	7.79

Appendix 6.2:
Pearson correlation coefficients (and significance levels) of elements extracted sequentially after the method of Hall (1996) (both sediment types and both treatments, n=8). These are the correlations on which the PCA analyses in Primer were based on.

Correlation Matrix NaOAc leach

		Fe	Mn	Al	Ca	S
Correlation						
	Mn	-.765				
	Al	.463	-.671			
	Ca	-.773	.924	-.573		
	S	-.445	.427	-.028	.539	
	Si	.202	.212	-.420	.096	.392
Sig. (1-tailed)						
	Mn	.014				
	Al	.124	.034			
	Ca	.012	.001	.069		
	S	.153	.146	.473	.084	
	Si	.316	.307	.150	.411	.169

Correlation Matrix 1M Hydroxylamine leach

		Fe	Mn	Al	Ca	S
Correlation						
	Mn	-.523				
	Al	-.547	.353			
	Ca	-.248	.189	.326		
	S	.416	-.399	-.143	-.374	
	Si	-.702	.211	.866	.013	-.123
Sig. (1-tailed)						
	Mn	.092				
	Al	.080	.196			
	Ca	.277	.327	.215		
	S	.153	.164	.368	.181	
	Si	.026	.308	.003	.488	.386

Correlation Matrix Pyro-phosphate leach

		Fe	Mn	Al	Ca	S
Correlation						
	Mn	-.728				
	Al	.792	-.454			
	Ca	-.450	.500	.090		
	S	-.367	.672	-.306	.093	
	Si	-.704	.143	-.763	.061	-.270
Sig. (1-tailed)						
	Mn	.020				
	Al	.010	.129			
	Ca	.132	.104	.415		
	S	.185	.034	.234	.413	
	Si	.026	.367	.014	.443	.259

Correlation Matrix $KClO_3$ leach

		Fe	Mn	Al	Ca	S
Correlation						
	Mn	.264				
	Al	-.366	.772			
	Ca	-.453	.026	.103		
	S	.998	.213	-.406	-.488	
	Si	.512	.930	.559	-.152	.467
Sig. (1-tailed)						
	Mn	.263				
	Al	.187	.012			
	Ca	.130	.476	.404		
	S	.000	.306	.159	.110	
	Si	.097	.000	.075	.360	.122

Correlation Matrix 0.25 M Hydroxylamine

		Fe	Mn	Al	Ca	S
Correlation						
	Mn	-.172				
	Al	-.494	-.314			
	Ca	-.311	.427	.135		
	S	.177	.650	-.603	-.256	
	Si	-.606	-.534	.802	.224	-.762
Sig. (1-tailed)						
	Mn	.342				
	Al	.107	.225			
	Ca	.227	.146	.375		
	S	.338	.041	.057	.271	
	Si	.055	.086	.008	.297	.014

Correlation Matrix Aqua Regia leach

		Fe	Mn	Al	Ca	S
Correlation						
	Mn	.818				
	Al	.888	.909			
	Ca	.089	.232	.128		
	S	-.685	-595	-.614	.148	
	Si	.402	.542	.514	-.307	-.185
Sig. (1-tailed)						
	Mn	.006				
	Al	.002	.001			
	Ca	.417	.290	.381		
	S	.030	.060	.053	.364	
	Si	.162	.083	.096	.230	.330

Appendix 6.3:

PRIMER raw results for Fe extractions

PCA
Principal Component Analysis

Worksheet

File: C:\My Documents\New PhD Project\Fe extractions (mean values).pri
Sample selection: All
Variable selection: 1-4,6,7 **(NaOAc extractions)**

Eigenvalues

PC	Eigenvalues	%Variation	Cum.%Variation
1	3.39	56.6	56.6
2	1.29	21.4	78.0
3	0.99	16.4	94.4
4	0.22	3.6	98.0
5	0.10	1.7	99.7

Eigenvectors
(Coefficients in the linear combinations of variables making up PC's)

Variable	PC1	PC2	PC3	PC4	PC5
Fe-NaOAc	-0.447	0.412	0.075	0.615	0.350
Mn-NaOAc	0.518	-0.053	0.101	0.440	-0.546
Al-NaOAc	-0.384	-0.192	-0.641	0.349	-0.442
Ca-NaOAc	0.513	-0.130	-0.067	0.504	0.448
S-NaOAc	0.314	0.257	-0.753	-0.224	0.280
Si-NaOAc	0.148	0.841	0.043	-0.048	-0.323

Principal Component Scores

Sample	SCORE1	SCORE2	SCORE3	SCORE4	SCORE5
Peat 3 wet	1.445	1.198	-1.626	-0.434	0.275
Floc 3 wet	1.304	1.582	0.499	0.367	-0.424
Peat 3 dry	2.054	-1.237	0.244	0.477	0.124
Floc 3 dry	1.361	-1.080	0.315	0.013	0.229
Peat 6 wet	-3.087	-0.102	-0.084	0.133	0.270
Floc 6 wet	-1.198	1.117	1.327	0.014	0.227
Peat 6 dry	-1.702	-0.642	-1.300	0.343	-0.372
Floc 6 dry	-0.178	-0.836	0.625	-0.913	-0.330

Outputs

Plot: Plot7

PCA
Principal Component Analysis

Worksheet

File: C:\My Documents\New PhD Project\Fe extractions (mean values).pri
Sample selection: All
Variable selection: 8-13 (**Pyro-P extractions**)

Eigenvalues

PC	Eigenvalues	%Variation	Cum.%Variation
1	3.10	51.7	51.7
2	1.62	26.9	78.6
3	1.06	17.6	96.2
4	0.15	2.6	98.8
5	0.05	0.9	99.7

Eigenvectors
(Coefficients in the linear combinations of variables making up PC's)

Variable	PC1	PC2	PC3	PC4	PC5
Fe-Pyro-P	-0.555	-0.071	0.113	0.157	0.469
Mn-Pyro-P	0.462	-0.388	-0.001	0.786	0.041
Al-Pyro-P	-0.469	-0.322	-0.334	0.134	-0.730
Ca-Pyro-P	0.231	-0.332	-0.774	-0.342	0.313
S-Pyro-P	0.277	-0.531	0.504	-0.472	-0.206
Si-Pyro-P	0.359	0.590	-0.152	-0.008	-0.324

Principal Component Scores

Sample	SCORE1	SCORE2	SCORE3	SCORE4	SCORE5
Peat 3 wet	-0.682	-0.845	-1.674	-0.493	0.186
Floc 3 wet	1.657	0.576	-1.017	0.654	0.204
Peat 3 dry	0.972	-1.882	-0.036	-0.118	-0.295
Floc 3 dry	1.453	-0.719	0.750	0.150	-0.008
Peat 6 wet	-3.004	1.083	-0.297	0.089	-0.109
Floc 6 wet	1.157	1.926	-0.101	-0.188	-0.313
Peat 6 dry	-2.167	-0.882	0.989	0.352	0.031
Floc 6 dry	0.616	0.744	1.386	-0.446	0.304

Outputs

Plot: Plot8

PCA
Principal Component Analysis

Worksheet

File: C:\My Documents\New PhD Project\Fe extractions (mean values).pri
Sample selection: All
Variable selection: 14-19 (**0.25 hydroxylamine extractions)**

Eigenvalues

PC	Eigenvalues	%Variation	Cum.%Variation
1	3.08	51.3	51.3
2	1.65	27.4	78.8
3	0.81	13.4	92.2
4	0.34	5.7	97.8
5	0.11	1.8	99.7

Eigenvectors
(Coefficients in the linear combinations of variables making up PC's)

Variable	PC1	PC2	PC3	PC4	PC5
Fe-0.25M HA	-0.313	0.478	0.539	0.481	0.247
Mn-0.25M HA	-0.315	-0.625	-0.067	0.306	-0.319
Al-0.25M HA	0.487	-0.065	-0.233	0.799	0.011
Ca-0.25M HA	0.138	-0.591	0.662	-0.041	0.318
S-0.25M HA	-0.488	-0.165	-0.452	0.091	0.705
Si-0.25M HA	0.555	-0.025	-0.090	-0.166	0.489

Principal Component Scores

Sample	SCORE1	SCORE2	SCORE3	SCORE4	SCORE5
Peat 3 wet	-0.357	-2.085	1.570	-0.011	-0.149
Floc 3 wet	2.218	-0.771	-0.286	0.454	0.212
Peat 3 dry	-2.724	-0.857	-0.920	0.050	0.438
Floc 3 dry	0.918	-0.053	-0.916	0.726	-0.286
Peat 6 wet	0.175	2.092	0.978	0.510	0.163
Floc 6 wet	1.880	0.405	-0.044	-1.020	0.311
Peat 6 dry	-2.166	1.133	0.242	-0.148	-0.160
Floc 6 dry	0.057	0.137	-0.623	-0.563	-0.529

Outputs

Plot: Plot9

PCA
Principal Component Analysis

Worksheet

File: C:\My Documents\New PhD Project\Fe extractions (mean values).pri
Sample selection: All
Variable selection: 20-25 (**1M hydroxylamine extractions**)

Eigenvalues

PC	Eigenvalues	%Variation	Cum.%Variation
1	3.02	50.3	50.3
2	1.32	21.9	72.3
3	1.14	19.0	91.3
4	0.35	5.9	97.1
5	0.17	2.8	99.9

Eigenvectors
(Coefficients in the linear combinations of variables making up PC's)

Variable	PC1	PC2	PC3	PC4	PC5
Fe-1M HA	-0.519	0.028	-0.105	0.667	0.307
Mn-1MHA	0.415	-0.380	0.449	-0.089	0.589
Al 1MHA	0.446	0.443	-0.222	0.364	0.469
Ca-1M HA	0.184	-0.193	-0.848	-0.267	0.143
S-1M HA	-0.330	0.633	0.097	-0.556	0.370
Si-1M HA	0.466	0.469	0.099	0.186	-0.426

Principal Component Scores

Sample	SCORE1	SCORE2	SCORE3	SCORE4	SCORE5
Peat 3 wet	0.726	-2.245	-0.984	0.331	0.096
Floc 3 wet	2.078	1.001	-0.281	0.058	0.653
Peat 3 dry	-0.525	-0.926	0.688	-0.960	0.284
Floc 3 dry	1.504	0.881	1.121	0.270	-0.083
Peat 6 wet	-2.197	0.330	-0.368	0.974	0.094
Floc 6 wet	0.507	0.916	-1.803	-0.513	-0.533
Peat 6 dry	-2.846	0.565	0.318	-0.347	0.081
Floc 6 dry	0.753	-0.523	1.309	0.187	-0.593

Outputs

Plot: Plot10

PCA
Principal Component Analysis

Worksheet

File: C:\My Documents\New PhD Project\Fe extractions (mean values).pri
Sample selection: All
Variable selection: 26-31 (**$KClO_3$ extractions**)

Eigenvalues

PC	Eigenvalues	%Variation	Cum.%Variation
1	2.93	48.9	48.9
2	2.29	38.2	87.1
3	0.73	12.2	99.3
4	0.04	0.7	100.0
5	0.00	0.0	100.0

Eigenvectors
(Coefficients in the linear combinations of variables making up PC's)

Variable	PC1	PC2	PC3	PC4	PC5
Fe-KClO3	-0.491	0.333	0.221	0.229	0.352
Mn-KClO3	-0.419	-0.454	0.097	0.358	-0.682
Al-KClO3	-0.121	-0.619	-0.317	0.351	0.604
Ca-KClO3	0.276	-0.287	0.895	0.074	0.175
S-KClO3	-0.480	0.361	0.172	0.251	0.076
Si-ClO3	-0.511	-0.296	0.105	-0.792	0.101

Principal Component Scores

Sample	SCORE1	SCORE2	SCORE3	SCORE4	SCORE5
Peat 3 wet	2.095	0.006	0.772	-0.105	-0.039
Floc 3 wet	0.439	-2.455	0.991	0.155	-0.001
Peat 3 dry	1.352	0.380	-0.870	-0.195	-0.033
Floc 3 dry	-0.975	-2.121	-1.149	0.021	0.025
Peat 6 wet	0.542	1.685	0.621	0.127	0.060
Floc 6 wet	-1.953	0.303	0.465	-0.360	0.028
Peat 6 dry	1.243	1.055	-0.929	0.161	0.016
Floc 6 dry	-2.744	1.148	0.099	0.196	-0.056

Outputs

Plot: Plot11

PCA
Principal Component Analysis

Worksheet

File: C:\My Documents\New PhD Project\Fe extractions (mean values).pri
Sample selection: All
Variable selection: 32-37 (**aqua regia extractions)**

Eigenvalues

PC	Eigenvalues	%Variation	Cum.%Variation
1	3.65	60.8	60.8
2	1.25	20.8	81.6
3	0.76	12.6	94.2
4	0.21	3.5	97.7
5	0.14	2.3	99.9

Eigenvectors
(Coefficients in the linear combinations of variables making up PC's)

Variable	PC1	PC2	PC3	PC4	PC5
Fe-AR	0.490	0.099	0.000	-0.352	0.789
Mn-AR	0.510	0.123	0.019	-0.137	-0.443
Al-AR	0.503	0.096	-0.183	-0.287	-0.405
Ca-AR	-0.005	0.829	-0.378	0.404	0.080
S-AR	-0.406	0.010	-0.647	-0.623	-0.038
Si-AR	0.287	-0.527	-0.636	0.473	0.095

Principal Component Scores

Sample	SCORE1	SCORE2	SCORE3	SCORE4	SCORE5
Peat 3 wet	-1.776	-0.141	0.410	-0.175	-0.180
Floc 3 wet	1.884	1.531	0.136	0.098	-0.509
Peat 3 dry	-1.410	-1.213	-0.923	0.712	-0.292
Floc 3 dry	2.981	-0.657	-1.130	-0.418	0.062
Peat 6 wet	-1.571	1.790	-0.785	0.101	0.515
Floc 6 wet	0.623	0.178	1.328	0.249	-0.027
Peat 6 dry	-1.922	-0.509	0.216	-0.782	-0.115
Floc 6 dry	1.191	-0.980	0.749	0.214	0.545

Outputs

Plot: Plot12

For correlations (Draftsman plots), see Appendix 6.2.